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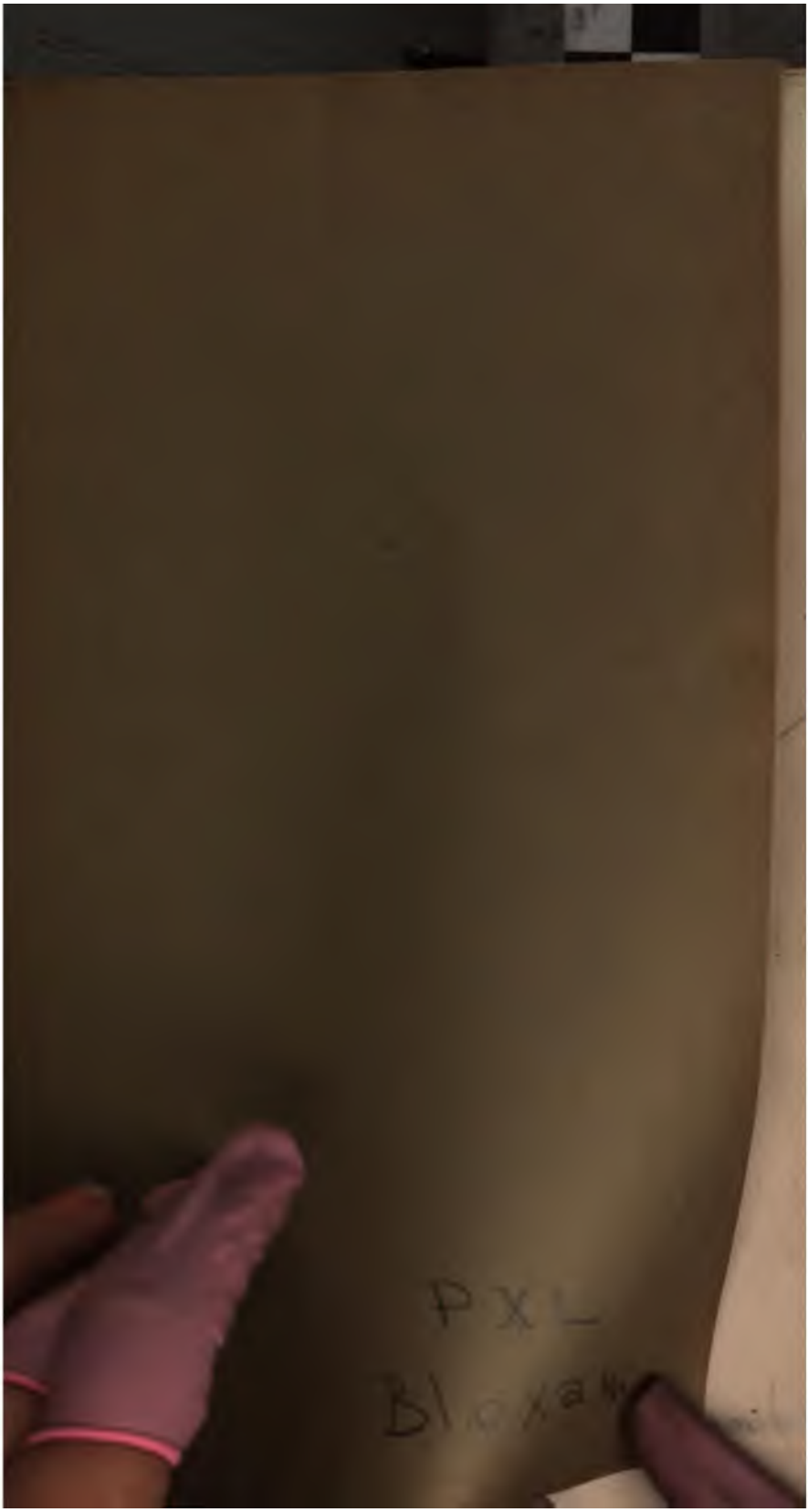

Chemistry - Systematic treatises 1867
(I.C)

CHEMISTRY

INORGANIC AND ORGANIC

WITH EXPERIMENTS

AND

A COMPARISON OF EQUIVALENT AND MOLECULAR FORMULÆ.

BY

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PREFACE.

At the present time, when there is so much difference of opinion as to the clearest mode of representing the constitution of chemical compounds and the changes in which they are involved, the author of a work on Chemistry is placed in a difficult position. Fully realising this, I should scarcely have ventured to undertake the task, but for the circumstance that, a third edition of "Abel and Bloxam's Handbook of Chemistry" being required, and my valued coadjutor not having leisure to devote to its preparation, it seemed to me a favourable opportunity for re-writing the handbook in such a form as to render it more useful to the general student.

The present work, therefore, is designed to give a clear and simple description of the elements and their principal compounds, and of the chemical principles involved in some of the most important branches of manufacture. Keeping this in view, I have employed as few technical terms as possible, especially at the commencement, so that the student may glide into Chemistry without having first to toil through a difficult chapter on the terminology of the science, which he can never appreciate until he has become acquainted with the examples which serve to illustrate its application.

Convinced, by experience, of the great assistance afforded to the learner by referring him to a simple illustrative experiment, I have introduced, generally in smaller type, a description, and in most cases a wood-engraving,* of the experiments which I have found most useful in illustrating lectures, hoping that these may prove of

* These were drawn by Mr Collings and engraved by Mr Hart, to whom I feel much indebted for their patient endeavours to represent faithfully the various forms of apparatus.

service in fixing the attention of the student, and may assist those who are desirous of performing such experiments for their own instruction, or for that of a class.

In explaining chemical changes by equations, I have, as a general rule, employed symbols representing combining weights (or equivalents), and not atoms, of the elements. Had the work been intended for advanced students, I should have hesitated to incur the reproach of obstinate conservatism, or of being behind the chemical spirit of the time, though even then, which of the more advanced systems was to be adopted would have been a very formidable question, for at present the different modes of representing chemical changes are almost as numerous as chemical writers.

When the atomic or molecular system of notation affords a clearer explanation, I have endeavoured to give the student the benefit of it, and this of course occurs most frequently in the department of Organic Chemistry, where the elements concerned in the formation of compounds are few, and atomic constitution becomes of greater importance. In such cases I have represented the *atoms* of elements by the barred symbols (Θ, Ɇ, &c.), and have adopted essentially the same atomic and molecular formulæ as have been employed by my colleague, Professor Miller, in the later editions of his "Elements of Chemistry."*

In general, English weights and measures, and Fahrenheit thermometric degrees, have been employed, as conveying more clearly to the beginner the absolute values expressed, since the mental effort of converting what must still be called the continental systems, slight though it be, might have the effect of diverting the attention of the reader from the chemical question under consideration. The various calculations have been conducted in the simplest arithmetical form, because the more compendious algebraical expressions are not so generally intelligible, and when the principle is once understood, a general algebraical formula for the calculation is easily constructed by the learner.

ial attention devoted to Metallurgy and some other

* myself under heavy obligation to Dr Miller's splendid volume on summaries which it contains having frequently spared me l memoirs.

branches of Applied Chemistry, will render the work useful to those who are being educated for employment in manufacture.

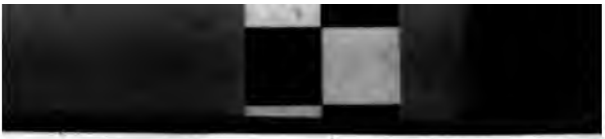
The military student will find more than the usual space allotted to the chemistry of the various substances employed in warlike stores.

In fine, it has been my endeavour to produce a Treatise on Chemistry sufficiently comprehensive for those studying the science as a branch of general education, and one which a student may peruse with advantage before commencing his chemical studies at one of the colleges or medical schools, where he will abandon it for the more advanced work placed in his hands by the professor. I am not without hope that this book may also be found useful in enabling the student who has acquired his knowledge of Chemistry with the help of the older system of notation in equivalents, to pass, should he deem it advisable, by an easy transition, into the use of atomic symbols and unitary formulæ.

C. L. B.

Woolwich, *January* 1867.

*** In the following pages, the smaller type contains not only the descriptions of experiments, but all such matter as would be of less importance to a student desiring only a general knowledge of the subject without going into details.



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INTRODUCTION.

1. CHEMISTRY describes the properties of the different particles of which all kinds of matter are composed, and teaches the laws which regulate their union with, or separation from, each other.

Matter is anything which possesses weight. Matter is chemically divided into two great classes—elements and compounds.

An ELEMENT is that which has not been found divisible into more than one kind of matter.

A COMPOUND consists of two or more elements held together by chemical attraction.

CHEMICAL ATTRACTION is the force which causes different kinds of matter to unite, in order to form a new kind of matter.

Chemical Combination is the operation of chemical attraction.

Chemical Decomposition is the separation of two or more kinds of matter previously held together by chemical attraction.

2. The elements known at present are sixty-four in number, and are divided into metallic and non-metallic elements.

The *Non-Metallic Elements* are (15)

Oxygen.	Sulphur	Fluorine.
Hydrogen.	Selenium.	Chlorine.
Nitrogen.	Tellurium.	Bromine.
Carbon.	Phosphorus.	Iodine.
Boron.	Arsenic.*	
Silicon.		

The *Metals* are (49)

Cæsium.	Aluminum.	Zinc.	Copper.	Mercury.
Rubidium.	Glucinum.	Nickel.	Bismuth.	Silver.
Potassium.	Zirconium.	Cobalt.	Lead.	Gold.
Sodium.	Thorinum.	Iron.	Thallium.	Platinum.
Lithium.	Yttrium.	Manganese.	Tin.	Palladium.
Barium.	Erbium.	Chromium.	Titanium.	Rhodium.
Strontium.	Terbium.	Cadmium.	Tantalum.	Ruthenium.
Calcium.	Cerium.	Uranium.	Molybendum.	Osmium.
Magnesium.	Lanthanum.	Indium.	Tungsten.	Iridium.
	Didymium.		Vanadium.	
	Niobium.		Antimony.	

The strict definition of a metal will be given hereafter.

Many of these elements are so rarely met with, that they have not

* In many English chemical works arsenic is classed among the metals, which it resembles *in some of its properties.*

received any useful application, and are interesting only to the professional chemist. This is the case with selenium and tellurium, among the non-metallic elements, and with a large number of the metals.

The following list includes those elements with which it is important that the general student should become familiar, together with the symbolic letters by which it is customary to represent them, for the sake of brevity, in chemical writings.

Non-Metallic Elements of practical importance (13).

Oxygen,	O	Sulphur,	S	Fluorine,	F
Hydrogen,	H	Phosphorus,	P	Chlorine,	Cl
Nitrogen,	N	Arsenic,	As	Bromine,	Br
Carbon,	C			Iodine,	I
Boron,	B				
Silicon,	Si				

Metallic Elements of practical importance (26).

Potassium,	K	(*Kalium.*)	Cadmium,	Cd	
Sodium,	Na	(*Natrium.*)	Uranium,	U	
Barium,	Ba		Copper,	Cu	(*Cuprum.*)
Strontium,	Sr		Bismuth,	Bi	
Calcium,	Ca		Lead,	Pb	(*Plumbum.*)
Magnesium,	Mg		Tin,	Sn	(*Stannum.*)
Aluminum,	Al		Titanium,	Ti	
Zinc,	Zn		Tungsten,	W	(*Wolframium.*)
Nickel,	Ni		Antimony,	Sb	(*Stibium.*)
Cobalt,	Co		Mercury,	Hg	(*Hydrargyrum.*)
Iron,	Fe	(*Ferrum.*)	Silver,	Ag	(*Argentum.*)
Manganese,	Mn		Gold,	Au	(*Aurum.*)
Chromium,	Cr		Platinum,	Pt	

The symbols represent definite relative proportions of the elements to which they are attached.

The values assigned to the symbols in the following list may be regarded as representing the relative *weights* in which they usually enter into chemical combination, and may be termed *combining weights* of the elements.

Hydrogen is taken as the unit, because its combining weight is less than that of any other known element.

*Combining Weights of the practically important Elements.**

Aluminum,	Al	13·7	Copper,	Cu	31·8	Phosphorus,	P	31·0
Antimony,	Sb	122·0	Fluorine,	F	19·0	Platinum,	Pt	98·6
Arsenic,	As	75·0	Gold,	Au	196·7	Potassium,	K	39·0
Barium,	Ba	68·5	Hydrogen,	H	1·0	Silicon,	Si	14·0
Bismuth,	Bi	210·0	Iodine,	I	127·0	Silver,	Ag	108·0
Boron,	B	11·0	Iron,	Fe	28·0	Sodium,	Na	23·0
Bromine,	Br	80·0	Lead,	Pb	103·5	Strontium,	Sr	43·8
Cadmium,	Cd	56·0	Magnesium,	Mg	12·2	Sulphur,	S	16·0
Calcium,	Ca	20·0	Manganese,	Mn	27·5	Tin,	Sn	59·0
Carbon,	C	6·0	Mercury,	Hg	100·0	Titanium,	Ti	25·0
[illegible]rine,	Cl	35·5	Nickel,	Ni	29·5	Tungsten,	W	92·0
[illegible]mium,	Cr	26·3	Nitrogen,	N	14·0	Uranium,	U	60·0
[illegible]alt,	Co	29·5	Oxygen,	O	8·0	Zinc,	Zn	32·8

[illegible]combining weigh[illegible] are not in all [illegible] the numbers [illegible]list, though sufficiently correct for all practical [illegible]ct. The small fractions have been omitted, in retained in the memory.

Although the 39 elements here enumerated are of practical importance, many of them derive their importance solely from their having met with useful applications in the arts. The number of elements known to play an important part in the chemical changes concerned in the maintenance of animal and vegetable life is very limited.

Elements concerned in the Chemical Changes taking place in Life.

Non-Metallic.		*Metallic.*	
Oxygen.	Sulphur.	Potassium.	Aluminum.
Hydrogen.		Sodium.	
Nitrogen.	Phosphorus.		Iron.
Carbon.		Calcium.	Manganese.
	Chlorine.	Magnesium.	
Silicon.	Iodine.		

These elements will, of course, possess the greatest importance for those who study Chemistry as a branch of general education, since a knowledge of their properties is essential for the explanation of the simplest chemical changes which are daily witnessed.

The student who takes an interest in the useful arts will also acquaint himself with the remainder of the 39 elements of practical importance, whilst the mineralogist and professional chemist must extend his studies to every known element.

By far the greater proportion of the various materials supplied to us by animals and vegetables consists of the four elements—oxygen, hydrogen, nitrogen, and carbon; and if we add to these the two most abundant elements in the mineral world, silicon and aluminum, we have the six elements composing the bulk of all matter.

3. Compound substances are commonly classified by the chemist into *Organic* and *Inorganic* compounds; and although it is impossible strictly to define the limits of each class, the division is a convenient one for the purposes of study.

Organic substances may be defined as those for which we are indebted to the operation of animal or vegetable life, such as starch, sugar, &c.

Inorganic substances are obtained from the mineral world without the intervention of life; as common salt, alum, &c.

Organic substances always contain carbon, generally also hydrogen and oxygen, and very frequently nitrogen.

)EF.—The compounds of oxygen with other elements are called
les.)
he act of combination with oxygen, or *oxidation*, like all other acts of
nical combination, is attended with the development of heat.* When
heat thus produced is sufficient to render the particles of matter
inous, the act of combination is styled combustion.
)EF.—*Combustion* is chemical combination attended with heat and
t.)

*Phosphorus, the only non-metal which combines with oxygen at the
nary temperature*, affords a good illustration of these propositions.
element, a solid at the ordinary temperature, is preserved in bottles
l with water, on account of the readiness with which the oxygen of
air combines with it. If a small piece of phosphorus be dried by
le pressure between blotting paper, and exposed to the air, its par-
s begin to combine at once with oxygen, and the heat thus developed
tly raises the temperature of the mass.
ow, *heat generally encourages chemical union*, so that the effect of
rise of temperature is to induce a more extensive combination of the
phorus with the oxygen, causing a greater development of heat in a
n time, until the temperature is sufficient to render the particles
iantly luminous, and a true case of combustion results—the combina-
of the phosphorus with oxygen, attended with production of heat
light.
)EF.—*Combustion in air* is the chemical combination of the elements
e combustible with the oxygen of the air, attended with develop-
of heat and light.)
a dry glass (fig. 1) be placed over
burning phosphorus, the thick
e smoke which proceeds from it
be collected in the form of snowy
s. These flakes are commonly
ed *anhydrous phosphoric acid*,†
are composed of one combining
ht of phosphorus (P = 31), and
combining weights of oxygen
8 × 5 = 40). This would be re-
nted by the formula PO_5.

Fig. 1.

the white flakes are exposed to the air for a short time they attract
ture and become little drops, which have a very sour or *acid* taste.
ubstances which have such a taste have been found also to be capable
anging the blue colour of *litmus*‡ to red, whence the chemist is in
abit of employing paper dyed with blue litmus for the recognition of
id. It must be remembered, however, that there are some acids
h, not being dissolved by water, have neither a sour taste nor the

hough this heat is not always perceptible by the thermometer or by the senses.
when chalk is dissolved in an acid, no heat is perceived, because all the heat attend-
e union of the lime with the acid is consumed in converting the carbonic acid from
lid chalk into a gas. To explain the manifestation of heat in the act of chemi-
mbination falls within the province of the physicist rather than of the chemist.
n writers attribute it to the motion of the molecules which compose the combining
s.

Anhydrous, or without water, from *αν*, negative, and *ὑδωρ*, water.
colouring matter prepared from a lichen, *Roccella tinctoria*; the cause of the
of colour will be more easily understood hereafter.

To demonstrate the brilliant combustion of phosphorus in oxygen, a piece not larger than a good-sized pea is placed in a little copper or iron cup upon an iron stand (fig. 3), and kindled by being touched with a hot wire (for even in pure oxygen spontaneous combustion cannot be ensured). The glass vessel having been previously filled with oxygen, and kept in a plate containing a little water, is placed over the burning phosphorus.*

Fig. 3. Phosphorus burning in oxygen.

It will be observed that the same white clouds of phosphoric acid are formed, whether phosphorus is burnt in oxygen or in air, exemplifying the fact that *a substance will combine with the same proportion of oxygen, whether its combustion*

* Would be of thin, well-annealed glass, and is sure to be broken if too large a vessel be employed

effected in pure oxygen or in atmospheric air. The apparent increase heat is due to the combustion of a greater weight of phosphorus in a ven time. The total heating effect produced by the combustion of a ven weight of phosphorus is the same whether air or pure oxygen be ployed.

8. Sulphur (*brimstone*) affords an example of a non-metallic elements hich will not enter into combination with oxygen until its temperature s been raised very considerably. When sulphur is heated in air, it on melts, and as soon as its temperature reaches 500° F. it takes fire, rning with a pale blue flame. If the burning sulphur be plunged into jar of oxygen, the blue light will become very brilliant, but the same t of combination takes place, one combining weight (16 parts) of sulphur iting with two combining weights ($8 \times 2 = 16$) of oxygen to form *sulurous acid* gas (SO_2), which may be recognised in the jar by the well-own suffocating smell of brimstone matches.

The experiment is most conveniently performed by heating the sulphur a *deflagrating spoon* (A, fig. 4), which is then plunged into the jar of ygen, its collar (B) resting upon the ck of the jar which stands in a plate ntaining a little water. The water abrbs a part of the sulphurous acid gas, d will be found capable of strongly redning litmus paper. It is possible to oduce, though not by simple combustion, compound of sulphur with three combing weights of oxygen (SO_3, anhydrous lphuric acid), showing that *a substance es not always take up its full share of ygen when burnt.*

Fig. 4.—Sulphur burning in oxygen.

The luminosity of the flame of sulphur far inferior to that of phosphorus, beuse, in the former case, there are no minute solid particles in the flame rresponding to those of the phosphoric acid produced in the combusn of phosphorus, and *no flame can emit a brilliant light unless it conins solid matter heated to incandescence.*

9. Carbon, also a non-metallic element, requires the application of a gher temperature than sulphur to induce it to enter into direct union th oxygen; indeed, perfectly pure carbon appears to require a heat apoaching whiteness to produce this effect. But charcoal (the carbon in hich is associated with not inconsiderable proportions of hydrogen and ygen) begins to burn in air at a much lower temperature, and if a piece wood charcoal, with a single spot heated to redness, be lowered into a r of oxygen, the adjacent particles will soon be raised to the combining mperature, and the whole mass will glow intensely, each combining eight (6) of carbon uniting with two combining weights ($8 \times 2 = 16$) of ygen to form *carbonic acid* (CO_2) gas, which will redden a piece of oistened blue litmus paper suspended in the jar, though much more ebly than either sulphurous or phosphoric acid, because it is a much eaker acid. It should be remembered that *carbon is an essential constient of all ordinary fuel, and carbonic acid is always produced by its comstion.*

It will be noticed that the combustion of the charcoal is scarcely at-

tended with flame, and when pure carbon (diamond, for example) is employed, no flame whatever is produced in its combustion, because carbon is not convertible into vapour, and all *flame is vapour or gas in the act of combustion*, hence *only those substances burn with flame which are capable of yielding combustible gases or vapours.*

10. The three examples of sulphur, phosphorus, and carbon sufficiently illustrate the tendency of non-metals to form acids by union with oxygen, which originally led to the adoption of its name derived from ὀξύς acid, and γεννάω, I produce. *All the non-metallic elements, except hydrogen and fluorine, are capable of forming acids by their union with oxygen.*

11. The metals, as a class, exhibit a greater disposition to unite directly with oxygen, though few of them will do so in their ordinary condition and at the ordinary temperature. Several metals, such as iron and lead, are superficially oxidised when exposed to air under ordinary conditions, but this would not be the case unless the air contained water and carbonic acid, which favour the oxidation in a very decided manner. Among the metals which are of importance in practice, five only are oxidised by exposure to dry air at the ordinary temperature, viz., potassium, sodium, barium, strontium, and calcium, the attraction of these metals for oxygen being so powerful that they must be kept under petroleum, or some similar liquid free from oxygen. On the other hand, three of the common metals, silver, gold, and platinum, have so little attraction for oxygen that they cannot be induced to unite with it directly, even at high temperatures.

If a lump of sodium be cut across with a knife, the fresh surfaces will exhibit a splendid lustre, but will very speedily tarnish by combining with oxygen from the air, which gives rise to a coating of *oxide of sodium* or *soda*, and this to some extent protects the metal beneath from oxidation. Even when the attraction of the sodium for oxygen is increased by the application of heat, it is long before the mass of sodium is oxidised throughout, unless the temperature be sufficiently high to convert a portion of the sodium into vapour, which bursts through the crust of soda, and burns with a yellow flame. If the spoon containing the sodium (see fig. 4) be now plunged into a jar of oxygen, the yellow flame will be far more brilliant.

One combining weight (23 parts) of sodium here combines with one combining weight (8) of oxygen to form soda (NaO), which remains in the spoon in a fused state. When the spoon is cool, it may be placed in water, which will dissolve the soda, acquiring a peculiar soapy feel and taste, as well as the property of restoring the blue colour to litmus paper which has been reddened by an acid. These properties are called *alkaline*, apparently because they were known to the early alchemists as being possessed by the ashes of plants (*potashes*) called *kali*.

(Def.—*A mineral* alkali* is a metallic oxide easily soluble in water, and capable of restoring the blue colour to litmus which has been reddened by an acid.)

If some diluted sulphuric acid be added drop by drop to a portion of the solution of soda, it will be found, after a certain quantity has been added, that the solution no longer feels soapy, and has a saline taste; if a piece of reddened litmus paper be wetted with it, the colour will remain unchanged, and the solution will not redden blue litmus paper. Such a

* There are other alkalies, such as ammonia and the vegetable alkalies, which are not *metallic oxides*.

solution is said to be neutral to test-papers, the alkali and the acid having neutralised each other.

(DEF.—*Neutralisation* is the destruction of the characteristic properties of an acid by an alkali or the converse.)

The liquid now contains a new substance called a *salt* (the strict definition of which will be given hereafter), and known as *sulphate of soda*, which would be represented in symbols by $NaO . SO_3$.*

Now, it will be remembered that soda (NaO) is composed of 23 parts by weight of sodium and 8 parts of oxygen; hence 31 parts by weight would be represented by NaO. And sulphuric acid (SO_3) is composed of 16 parts by weight of sulphur, and (8×3) 24 parts of oxygen, so that SO_3 represents 40 parts by weight, and the combining weights of soda and (anhydrous) sulphuric acid are respectively 31 and 40.

(RULE.—*The combining weights of compounds are obtained by adding together the weights represented by their symbols.*)

All acids would not have neutralised the properties of the alkali, in the above experiment, so completely as sulphuric acid; thus carbonic acid would never entirely destroy the property of the soda to restore the blue colour to reddened litmus, although it would very considerably modify its other properties; the solution of soda itself is capable of corroding the skin and textile fabrics, whence its old name of *caustic* soda, but when combined with carbonic acid, to form *carbonate of soda*, it loses these properties, and becomes what the older chemists called a *mild alkali*. Even the weakest acids possess this property of partially neutralising the alkalies.

(DEF.—*An acid* is a compound body which is capable of neutralising an alkali, either partly or entirely.)

12. Zinc will serve as an example of a metal which has no disposition to enter into combination with oxygen at the ordinary temperature,† but which is induced to unite with it by a very moderate heat. If a little zinc (*spelter*) be melted in a ladle or crucible, and stirred about with an iron rod, it burns with a beautiful greenish flame produced by the union of the vapour of zinc with the oxygen of the air. But the combustion is far more brilliant if a piece of zinc-foil be made into a tassel (fig. 5), gently warmed at the end, dipped into a little flowers of sulphur, kindled, and let down into a jar of oxygen, when the flame of the burning sulphur will ignite the zinc, which burns with great brilliancy. On withdrawing what remains of the tassel after the combustion is over, it will be found to consist of a friable‡ mass, which has a fine yellow colour while hot, and becomes white as it cools. This is the *oxide of zinc* (ZnO), formed by the union of one combining weight (32·8 parts) of zinc with one combining weight (8 parts) of oxygen.

Fig. 5.—Zinc burning in oxygen.

The oxide of zinc does not possess the properties of an acid or an alkali, but belongs to another class of compounds termed *bases*, which are not

* In expressing by symbols a compound of two or more compounds, they are always separated from each other by a full stop.

† Unless water and carbonic acid be present, as in common air.

‡ *Friable, easily crumbled or disintegrated.*

soluble in water as the alkalies are, but, like them, are capable of neutralising, either partly or entirely, the acids. Thus, if the oxide of zinc were added to diluted sulphuric acid as long as the acid would dissolve it, the well-known corrosive properties of the acid would be destroyed, although it would still retain the power of reddening blue litmus, and the solution would now contain a new substance, or salt, called *sulphate of oxide of zinc** ($ZnO . SO_3$).

(Def.—*A base* is a compound body which is capable of neutralising an acid, either partly or entirely.)

It will be observed that an alkali is only a particular species of base, and might be defined as a base which is very soluble in water.

(Def.—*A salt* is a compound body containing an acid in combination with a base, or a metal in combination with a *salt-radical*.† *Examples.*—Nitrate of potash ($KO . NO_5$) composed of (anhydrous) nitric acid (NO_5) and potash (KO). Chloride of sodium (NaCl).)

(Def.—*A salt-radical* or *halogen* is a substance which forms an acid when combined with hydrogen. *Examples.*—Chlorine, which forms hydrochloric acid (HCl); Cyanogen (C_2N), which forms hydrocyanic acid (HC_2N).)

13. Iron, in its ordinary form, like zinc, is not oxidised by *dry* air or oxygen at the ordinary temperature; but if it be heated even to only 500° F. a film of oxide of iron forms upon its surface, and as the heat is increased the thickness of the film increases, until eventually it becomes so thick that it can be detached by hammering the surface, as may be seen in a smith's forge. If an iron rod as thick as the little finger be heated to whiteness at the extremity, and held before the nozzle of a powerful bellows, it will burn brilliantly, throwing off sparks and dropping melted oxide of iron. If a stream of oxygen be substituted for air, the combustion is of the most brilliant description. A watch-spring (iron combined with about 1 per cent. of carbon) may be easily made to burn in oxygen by heating it in a flame till its elasticity is destroyed, and coiling it into a spiral (A, fig. 6), one end of which is fixed, by means of a cork, in the deflagrating collar B; if the other end be filed thin and clean, dipped into a little sulphur, kindled, and immersed in a jar of oxygen (C) standing in a plate of water, the burning sulphur will raise the iron to the point of combustion, and the spring will be converted into molten drops of oxide.

Fig. 6.—Watch-spring burning in oxygen.

The black oxide of iron formed in all these cases is really a combination of two distinct oxides of iron, one of which contains one combining weight of iron (28 parts) and one (8 parts) of oxygen, and would be written FeO, whilst the other contains two combining weights (56) of iron and three (24) of oxygen, expressed by the formula Fe_2O_3. To distinguish them, the former is usually called *protoxide* of iron (πρῶτος, first), and the

* For the sake of brevity, it is usual to omit *oxide of* in designating salts. Thus sulphate of copper means sulphate of *oxide of* copper, nitrate of silver means nitrate of *oxide of* silver.

† *Salts of this description* are termed *haloid salts*, because they belong to the same class as sea-salt (NaCl), *from* ἅλς, the sea.

latter *sesquioxide* (in allusion to the ratio of one and a-half to one between the oxygen and the metal).* The sesquioxide of iron combined with water constitutes ordinary rust.

The black oxide usually contains one combining weight of each oxide, so that it would be written $FeO.Fe_2O_3$, or Fe_3O_4. It is powerfully attracted by the magnet, and is often called magnetic oxide of iron. The abundant magnetic ore of iron, of which the *loadstone* is a variety, has a similar composition.

Iron in a very fine state of division will take fire spontaneously in air as certainly as phosphorus. *Pyrophoric* iron can be obtained (by a process to be described hereafter) as a black powder, which must be preserved in sealed tubes. When the tube is opened, and its contents thrown into the air, oxidation takes place, and is attended with a vivid glow. In this case the red sesquioxide of iron is produced instead of the black oxide.

Both these oxides of iron are capable of neutralising, or partially neutralising, acids, and are therefore basic oxides or bases, like the oxides of zinc and sodium obtained in previous experiments. So general is the disposition of metals to form oxides of this class, that it may be regarded as one of the distinguishing features of a metal, for no non-metal ever forms a base with oxygen.

(DEF.—*A metal* is an element capable of forming a base† by combining with oxygen, or a salt by combining with a salt-radical.)

Many metals are capable also of forming acids with oxygen; thus, tin forms stannic acid (SnO_2), antimony forms antimonic acid (SbO_2), and it is always found that the acid oxide of a metal contains a larger proportion of oxygen than any of the other oxides which the metal may happen to form.

14. There is a third class of oxides, termed the *indifferent oxides*, because they are neither acids nor bases; such oxides may be formed either by non-metals or metals; thus water (HO), the oxide of hydrogen, is an indifferent oxide, and the black oxide or binoxide of manganese (MnO_2) is an example of an indifferent metallic oxide. It will be seen hereafter that the oxides of the non-metals are generally acids, and that when a metal combines with oxygen in several proportions, the oxides containing the smallest proportion of oxygen are usually bases, whilst those containing the largest proportion are acids, and the indifferent oxides contain an intermediate proportion of oxygen. The following list of the oxides of manganese will exemplify this, and will illustrate the names commonly bestowed upon oxides in order to indicate the proportion of oxygen which they contain:—

Protoxide of Manganese, . .	MnO,	Strong Base.
Sesquioxide of ,, . .	Mn_2O_3	Weak Base.
Binoxide, Peroxide,‡ of ,, . .	MnO_2	Indifferent.
Manganic Acid, ...	MnO_3	
Permanganic Acid, . . .	Mn_2O_7	

15. *Preparation of Oxygen.*—For almost all the useful arts in which uncombined oxygen is required, the diluted gas contained in atmospheric

* The terms ferrous and ferric oxide are now very often substituted for protoxide and sesquioxide of iron.

† The metal tungsten appears at present to be an exception to this rule, no well-defined basic oxide of this metal being known.

‡ *A peroxide is the highest oxide which does not* possess acid properties.

air is sufficient, since the nitrogen mixed with it does not interfere with its action.

From atmospheric air pure oxygen was first obtained by Lavoisier towards the end of the last century. His process is far too tedious to be employed as a general method of preparing oxygen, but it affords a very good example of the relation of heat to chemical attraction. Some mercury was poured into a glass flask with a long narrow neck, which was placed in a sand-bath, so that its temperature might be constantly maintained at about 660° F. for several weeks. The mercury boiled, and a portion of it was converted into vapour, which condensed in the neck of the flask and ran back again. Eventually the mercury was converted into a red powder, having combined with the oxygen of the air (or undergone *oxidation*) to form the *red oxide of mercury*. The nitrogen of the air does not enter into combination with the mercury.

By heating this oxide of mercury to a temperature approaching a red heat (about 1000° F.) it is decomposed into mercury and oxygen gas ($HgO = Hg + O$).

It is very generally found, as in this instance, that heat of moderate intensity will favour the operation of chemical attraction, whilst a more intense heat will annul it.

For the purpose of experimental demonstration, the decomposition of the oxide of mercury may be conveniently effected in the apparatus represented by fig. 7, where the oxide is placed in the German glass tube A, and heated by the Bunsen's

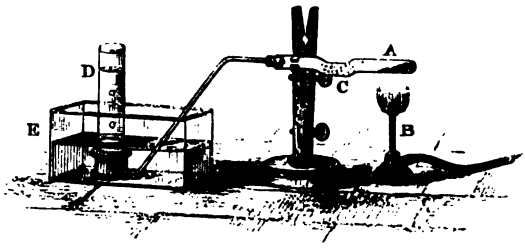


Fig. 7.—Preparation of oxygen from oxide of mercury.

gas-burner B, the metallic mercury being condensed in the bend C, and the oxygen gas collected in the gas cylinder D, filled with water, and standing upon the bee-hive shelf of the *pneumatic trough* E. It may be identified by its property of kindling into flame the spark left at the end of a wooden match. If the heat be continued for a sufficient length of time, the whole of the oxide of mercury will disappear, being resolved into its elements. In technical language, the mercury is said to be *reduced*.

Upon the first application of heat, the red oxide suffers a physical change, in consequence of which it becomes black; but its red colour returns again if it be allowed to cool.

Although processes have lately been devised for obtaining a supply of unmixed oxygen at a cheap rate from the atmosphere, the demand for the gas is as yet so small that they have not been carried out on a large scale.

16. The only other natural source from which it has been found convenient to prepare pure oxygen is a black mineral composed of manganese and oxygen. It is found in some parts of England, but much more

ıntly in Germany and Spain, whence it is imported for the use of acher and glass-maker. Its commercial name is *manganese*, but it vn to chemists as *binoxide of manganese* (MnO_2), and to minera- by several names designating different varieties. The most signi- of these names is *pyrolusite*, referring to the facility with which it decomposed by heat (πυρ, fire, and λυω, to loosen).

of the cheapest methods of preparing oxygen consists in heating ragments of this black oxide of manganese in an iron retort, placed od fire, the gas being collected in jars filled with water, and stand- on the shelf of the pneumatic trough, or in a gas-holder or gas-bag, r quantities are required.

attraction existing between manganese and oxygen is too powerful w the metal to part with the whole of its oxygen when heated, so ly one-third of the oxygen is given off in the form of gas, a brown of manganese being left in the retort.*

By far the most convenient source of oxygen, for general use in the ory, is the artificial salt called *chlorate of potash*, which is largely ıctured for fireworks, percussion- nposition, &c. If a few crystals salt be heated in a test-tube over t-lamp (fig. 8), it soon melts to a iquid, which presently begins to m the disengagement of bubbles gen, easily recognised by intro- a match with a spark at the end e upper part of the tube. If the of heat be continued until no more is given off, the residue in the ill be the salt termed chloride of ım.

Fig. 8.

chlorate of potash ($KO.ClO_5$) is composed of potash (KO) and acid (ClO_5). If the potash were uncombined with chloric acid, ould be quite incapable of decomposing it, but chlorine has a more ul attraction for potassium than even oxygen has at a high tem- e; and accordingly, when the salt is heated, union takes place n the potassium and the chlorine, whilst the whole of the oxygen lled in the form of gas, a result expressed by the equation

$$\underset{\text{Chlorate of potash.}}{KO\,.\,ClO_5} = \underset{\text{Chloride of potassium.}}{KCl} + O_6.$$

scertain what quantity of oxygen would be furnished by a given weight of of potash, the combining weights must be brought into use. Referring to e of combining weights (p. 2), it is found that K = 39, O = 8, and ·5; hence the combining weight of chlorate of potash is easily calculated.

One combining weight of potassium, . .	39
,, ,, chlorine, . .	35·5
Six combining weights of oxygen, . .	48
$KO\,.\,ClO_5 =$	122·5

at 122·5 grains of chlorate of potash would yield 48 grains of oxygen.

xpressed in the form of an equation: $\underset{\text{Black oxide of manganese.}}{3\,MnO_2} = \underset{\text{Brown oxide of manganese.}}{Mn_3\,O_4} + O_2.$

If it be required to know what would be the measure or volume of this oxygen at the ordinary atmospheric temperature (60° F.) and pressure (30 inches barometer), it must first be known that 31 grains of air under those conditions would occupy 100 cubic inches. Then, knowing (5) the specific gravity of oxygen to be 1·1057, the proportion—

1	:	1·1057	::	31	:	x
Spec. gr. (or weight of 1 vol.) of air,		Spec. gr. (or weight of 1 vol.) of oxygen,		Weight of 100 cub. in. of air,		Weight of 100 cub. in. of oxgyen,

gives us 34·28 grains for the weight of 100 cub. in. of oxygen.

(RULE.—*To find the weight of* 100 *cub. in. of a gas at* 60° *F. and* 30 *in. Bar., multiply its specific gravity by* 31).

Then	34·28	:	100	::	48	:	140
	Grs. of Oxygen.		Cub. In.		Grs. of Oxygen.		Cub. In.

Hence it is found that 122·5 grains of chlorate of potash would give 140 cub. in. of oxygen measured at 60° F. and 30 in. Bar.

If one gallon (277·276 cub. in.) of oxygen be required, 242·6 grains of chlorate of potash must be used, or rather more than half an ounce.

Since the complete decomposition of the chlorate of potash alone requires a more intense heat than a glass vessel will usually endure, it is customary in preparing oxygen for chemical purposes to facilitate the decomposition of the chlorate by mixing it with about one-fifth of its weight of powdered black oxide of manganese, when the whole of the oxygen is given off at a comparatively low temperature, though the oxide of manganese itself suffers no change, and its action has not yet received any explanation which is quite satisfactory.

Fig. 9 shows a very convenient arrangement for preparing and collecting oxygen for the purpose of demonstrating its relations to combustion. A is a Florence flask,

Fig. 9.—Preparation of oxygen.

in which the glass tube B is fixed by a perforated cork. C is a tube of vulcanised india-rubber. The gas-jar is filled with water, and supported upon a bee-hive shelf made of earthenware. If pint gas-jars be employed, 300 grains of the chlorate of potash, mixed with 60 grains of binoxide of manganese, will furnish a sufficient supply of gas for the ordinary experiments. The heat must be moderated according to the rate at which the gas is evolved, and the tube C must be taken out of the water before the lamp is removed, or the contraction of the gas in cooling will suck the water back into the flask. The first jar of gas will contain the air with which the flask was filled at the commencement of the experiment. The oxygen obtained will have a slight smell of chlorine.

OZONE.

18. OZONE is the name given to a substance of the true nature of which there is *still some doubt, as it has never* been obtained in a pure state, but which is pretty *generally believed to be* oxygen in a peculiar condition, much more disposed to com-

bine directly with other substances at the ordinary temperature than common oxygen, and possessed of a peculiar odour, whence it derives its name (ὄζω, *to smell*). Oxygen appears to be capable of assuming this *ozonised* condition under various circumstances, the principal of which are, the passage of silent electric discharges,* and the contact with substances (such as phosphorus) undergoing slow oxidation in the presence of water. A minute proportion of the oxygen obtained in the decomposition of water by the galvanic current also exists in the ozonised condition, as may be perceived by its odour.

The use of Siemens' induction tube (fig. 10) affords the readiest method of

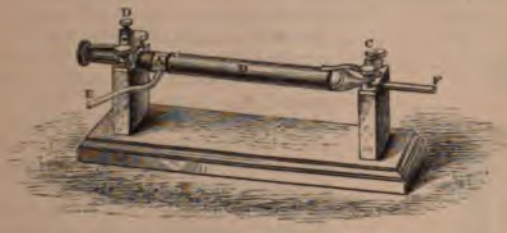


Fig. 10.—Tube for ozonising air by induction.

demonstrating the characteristic properties of ozone. This apparatus consists of a tube (A) coated internally with tin-foil (or silvered on the inside), and surrounded with another tube (B) which is coated with tin-foil on the outside. When the inner and outer coatings are placed in connexion with the wires of an induction coil by means of the screws (C D), and a stream of air or oxygen is passed through (E) between the two tubes, a strong odour is perceived at the orifice (F).

One of the best chemical tests for ozone is a damp mixture of starch with iodide of potassium. 100 grains of starch are well mixed in a mortar with a measured ounce of cold water, and the mixture is slowly poured into five ounces of boiling water in a porcelain dish, with occasional stirring. The thin starch-paste thus obtained is allowed to cool, and a few drops of solution of pure iodide of potassium are added, the mixture being well stirred with a glass rod. If this mixture be brushed over strips of white cartridge paper, these will remain unchanged in ordinary air; but when they are exposed to ozonised air (such as that which has passed through the induction tube), they will immediately assume a blue colour. The ozonised oxygen being more active, or endowed with more powerful chemical attractions than ordinary oxygen, abstracts the potassium from the iodide of potassium (KI), and sets free the iodine, which has the specific property of imparting a blue colour to starch. The intensity of the blue tint is proportionate to the quantity of iodine liberated, and therefore to that of the ozonised oxygen present, and hence, by reference to a standard scale of colours previously agreed upon, the ozone may be expressed in degrees. The result, however, is affected by so many trifling circumstances, that it is doubtful whether such determinations of the quantity of ozone are to be considered trustworthy. If the ozonised air issuing from F be passed into a solution of indigo (*sulphindigotic acid* largely diluted) the blue colour will soon disappear, since the ozone oxidises the indigo, and gives rise to products which, in a diluted state, are nearly colourless. Ordinary oxygen is incapable of bleaching indigo in this manner. If the ozone is passed through a tube of vulcanised caoutchouc, this will soon be perforated by the corrosive effect of the ozone, whilst ordinary oxygen would be without effect upon it.

If the ozone from F be made to pass slowly through a glass tube heated in the centre by a spirit-lamp, it will be found to lose its power of affecting the iodised starch-paper, the ozone having been reconverted into ordinary oxygen under the influence of heat. A temperature of 300° F. is sufficient to effect this change. It has been observed that a given volume of oxygen diminishes when a portion of it is converted into ozone by the silent electric discharge, and that it regains its original

* *It is the odour of ozone which is perceived in* working an ordinary electrical machine.

volume when the ozone is reconverted by heat, proving that the ozonised form of oxygen is denser, or occupies less space than the ordinary form.

By placing a freshly-scraped stick of phosphorus (scraped under water to avoid inflammation) at the bottom of a quart bottle, with enough water to cover half of it, and loosely covering the bottle with a glass plate, enough ozone may be accumulated in a few minutes to be readily recognised by the odour and the iodised starch. A plausible explanation of this production of ozone during the slow oxidation of phosphorus in the presence of water will be found under the head of *peroxide of hydrogen*.

If a few drops of ether (C_4H_5O) be poured into a quart beaker (fig. 11), taking care to avoid the vicinity of a flame, and pieces of iodised starch-paper and blue litmus paper be suspended upon a glass rod laid across the mouth of the beaker, they will be found unaffected by the mixture of ether vapour and air; but if a hot glass rod be plunged into the beaker, the heated ether vapour will undergo oxidation, producing acid vapours, which redden the blue litmus, whilst the formation of ozone will be indicated by the blue iodised starch (see *peroxide of hydrogen*).*

Fig. 11.

Ozone has attracted much notice, because a minute proportion of the oxygen in the atmosphere appears sometimes to be present in this form, and its active properties have naturally led to the belief that it must exercise some influence upon the sanitary condition of the air. This idea is encouraged by the circumstance that no indications of ozone can be perceived in crowded cities, where there are so many oxidisable substances to consume the active oxygen, whilst the air in the open country and at the sea-side does give evidence of its presence. Some chemists assert that their experiments have demonstrated the very important fact that a portion of the oxygen developed by growing plants is in the ozonised form.

The investigations into the true nature of ozone have given rise to interesting speculations with respect to the molecular constitution of oxygen, which will be noticed in the article upon *peroxide of hydrogen*.

Atmospheric Air.

19. Atmospheric air consists chiefly of a mixture of nitrogen with one-fifth of its volume of oxygen, and very small proportions of carbonic acid and ammonia. Vapour of water is of course always present in the atmosphere in varying proportions. Since the atmosphere is the receptacle for all gaseous emanations, other substances may be discovered in it by very minute analysis, but in proportions too small to have any perceptible influence upon its properties. Thus marsh-gas or light carburetted hydrogen, sulphuretted hydrogen, and sulphurous acid, can often be traced in it, the two last especially in or near towns.

Although the proportion of oxygen in the air at a given spot may be much diminished, and that of carbonic acid increased, by processes of oxidation (such as respiration and combustion) taking place there, the operation of wind and of diffusion so rapidly mixes the altered air with the immensely greater general mass of the atmosphere, that the variations in the composition of air in different places are very slight. Thus it has been found that the proportion of oxygen in the air in the centre of Manchester was, at most, only 0·2 per cent. below the average.

* The oxygen obtained by the action of warm sulphuric acid on binoxide of barium *resembles ozone in its* odour and action on the iodised starch-paper.

The proportions in which the oxygen and nitrogen are generally present in atmospheric air are—

	Volumes.	Weights.
Nitrogen, ...	79·19	76.99
Oxygen, ...	20·81	23·01
	100·00	100·00

The proportion of aqueous vapour may be stated, on the average, as 1·4 per cent. by volume, or 0·87 per cent. by weight of the air. The carbonic acid may be generally estimated at 0·04 per cent. by volume, or 0·06 per cent. by weight of the air.

The relative proportions of oxygen and nitrogen in air may be exhibited by suspending a stick of phosphorus upon a wire stand (A, fig. 12) in a measured volume of air confined over water. The cylinder (B) should have been previously divided into five equal spaces by measuring water into it, and each space marked by a thin line of Brunswick black. After a few hours, the phosphorus will have combined with the whole of the oxygen to form phosphorous acid, which is absorbed by the water, leaving four of the spaces occupied by nitrogen.

Fig. 12.

The same result may be arrived at in a much shorter time by burning the phosphorus in the confined portion of air.

A fragment of phosphorus, dried by careful pressure between blotting paper, is placed upon a convenient stand (A, fig. 13) and covered with a tall jar, having an opening at the top for the insertion of a well-fitting stopper (which should be greased with a little lard), and divided into seven parts of equal capacity. The jar should be placed over the stand in such a manner that the water may occupy the two lowest spaces into which the jar is divided. The stopper of the jar is furnished with a hook, to which a piece of brass chain (B) is attached, long enough to touch the phosphorus when the stopper is inserted. The end of this chain is heated in the flame of a lamp, and the stopper tightly fixed in its place. On allowing the hot chain to touch the phosphorus, it bursts into vivid combustion, filling the jar with thick white fumes, and covering its sides, for a few moments, with white flakes of phosphoric acid. At the commencement of the experiment, the water in the jar will be depressed, in consequence of the expansion of the air, due to the heat produced in the burning of the phosphorus, but, presently, when the combustion begins to decline, the water again rises, and continues to do so until it has ascended to the line (C), so as to occupy the place of one-fifth of the air employed in the experiment. The phosphorus will then have ceased to burn, the white flakes upon the sides of the jar will have acquired the appearance of drops of moisture, and the fumes will have gradually disappeared, until, in the course of half-an-hour, the air remaining in the jar will be as clear and transparent as before, the whole of the phosphoric acid having been absorbed by the water. The jar should now be sunk in water, so that the latter may attain to the same level without as within the jar. On removing the stopper, it will be found that the nitrogen in the jar will no longer support the combustion of a taper.

Fig. 13.

In *the rigidly accurate determination of the* relative proportions of oxygen and

nitrogen in the air, it is, of course, necessary to guard against any error arising from the presence of the water, carbonic acid, and ammonia. With this view, Dumas and Boussingault, to whom we are chiefly indebted for our exact knowledge of the composition of the air, caused it to pass through a series of tubes (A, fig. 14) containing potash, in order to remove the carbonic acid, then through a second series (B), containing sulphuric acid, to absorb the ammonia and water; the purified air then passed through a glass tube (C) filled with bright copper heated to redness in a charcoal furnace, which removed the whole of the oxygen, and the nitrogen passed into the large globe (N).

Both the tube (containing the copper) and the globe were carefully exhausted of air and accurately weighed before the experiment; on connecting the globe and the tube with the purifying apparatus, and slowly opening the stop-cocks, the pressure of the external air caused it to flow through the series of tubes into the globe destined to receive the nitrogen. When a considerable quantity of air had passed in, the stop-cocks were again closed, and, after cooling, the weight of the globe was accurately determined. The difference between this weight and that of the empty globe before the experiment, gave the weight of the nitrogen which had entered the globe, but this did not represent the whole of the nitrogen contained in the analysed air, for the

Fig. 14.—Exact analysis of air.

tube containing the copper had, of course, remained full of nitrogen at the close of the experiment. This tube having been weighed, was attached to the air-pump, the nitrogen exhausted from it, and the tube again weighed; the difference between the two weighings furnished the weight of the nitrogen remaining in the tube, and was added to the weight of that received in the globe. The oxygen was represented by the increase in the weight of the exhausted tube containing the copper, which was partially converted into oxide of copper, by combining with the oxygen of the air passed through it.

The calculation of the result of the analysis is here exemplified:—

Weight of	Grains.	
Globe (N) with nitrogen (at the conclusion), . .	8076	
Exhausted globe (at the commencement), . . .	8000	
Nitrogen received into the globe, . . .	76	
Tube (C) with residual nitrogen (at the conclusion), .	2574	
Exhausted tube (at the conclusion), ...	2573	
Nitrogen remaining in the tube, . . .	1	
Add nitrogen received into the globe, . .	76	
Total nitrogen in the air analysed, . .	77	
Exhausted tube (C) with oxidised copper (at the conclusion),		2573
,, ,, metallic copper (at the commencement),		2550
Oxygen in the air analysed, ...		23

The ratio of the oxygen to the nitrogen, therefore, is that of 23N : 77O, or 1N : 8.347O. 100 parts by weight of the air purified from water, carbonic acid, and ammonia, contain 77 parts of nitrogen and 23 parts of oxygen.

20. The nitrogen remaining after the removal of the oxygen from air in the above experiments, was so called on account of its presence in nitre (saltpetre $KO.NO_5$). In physical properties it resembles oxygen, but is somewhat lighter than that gas, its specific gravity being 0·9713.

This difference in the specific gravities of the two gases is well exhibited by the arrangement shown in fig. 15. A jar of oxygen (O) is closed with a glass *plate, and placed* upon the table. A jar of nitrogen (N), also closed with a glass

laced over it, so that the two gases may come in contact when the glass removed. The nitrogen will float for some seconds above the oxygen, lighted taper be quickly introduced through of the upper jar, it will be extinguished in hrough the nitrogen, and will be rekindled when it reaches the oxygen in the lower jar.

Fig. 15.

ght at first sight appear surprising that nd nitrogen, though of different specific , should exist in uniform proportions in s of the atmosphere, unless in a state of l combination, but an acquaintance with perty of diffusion (see *Hydrogen*) pos- y gases teaches us that *gases will mix h other in opposition to gravitation, and xed will always remain so.*

air is simply a mechanical mixture of its nt gases is amply proved by the circum- hat it possesses all the properties which e predicted for a *mixture* of these gases proportions; whilst the essential feature *mical compound* is, that its properties e foreseen from those of its constituents.

bsence of active chemical properties is a very striking feature of , and admirably adapts it for its function of diluting the oxygen tmosphere. There is no direct test by which nitrogen gas can be ed, so that the chemist is obliged to prove that the gas under ex- n does not possess the characters of any other gas with which he inted before he can pronounce it to be nitrogen.

hemical relations of air to animals and plants will be more appro- discussed hereafter. (See *Carbonic Acid, Ammonia.*)

HYDROGEN.

Unlike oxygen, hydrogen is very rarely found uncombined in nature. bination it occurs abun- n water and in all ani- l vegetable substances. ieties of fuel contain n. It is always pro- rom the first of these

r is composed of the ements, hydrogen and held together by che- ttraction. To separate ements, that is, to de- or *analyse* water, we overcome the chemical n between them, which effected by causing the s of water to transmit t of voltaic electricity.

Fig. 16.—Electrolysis of water.

ngement for decomposing water by the voltaic or galvanic battery *sented in fig. 16.*

The glass vessel A contains water, to which a little sulphuric acid has been added to increase its power of conducting electricity, for pure water conducts so imperfectly that it is decomposed with great difficulty. B and C are platinum plates bent into a cylindrical form, and attached to stout platinum wires, which are passed through corks in the lateral necks of the vessel A, and are connected by binding screws with the copper wires D and E, which proceed from the galvanic battery G. H and O are glass cylinders with brass caps and stop-cocks, and are enlarged into a bell-shape at their lower ends for the collection of a considerable volume of gas. These cylinders are filled

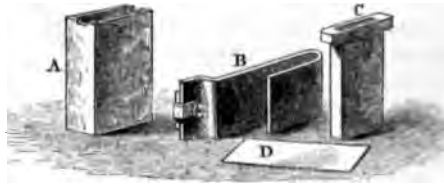


Fig. 17.

with the acidulated water, by sucking out the air through the opened stop-cocks; on closing these, the pressure of the air will of course sustain the column of water in the cylinders. G is a Grove's battery, consisting of five cells or earthenware vessels (A, fig. 17) filled with diluted sulphuric acid (one measure of oil of vitriol to four of water). In each of these cells is placed a bent plate of zinc (B), which has been *amalgamated* or rubbed with mercury (and diluted sulphuric acid) to protect it from corrosion by the acid when the battery is not in use. Within the curved portion of this plate rests a small flat vessel of unglazed earthenware (C), filled with strong nitric acid, in which is immersed a sheet of platinum foil (D). The platinum (D) of each cell is in contact, at its upper edge, with the zinc (B) in the adjoining cell (fig. 18), so that at one end (P, fig. 16) of the battery there is a free platinum plate, and at the other (Z) a free zinc plate. These plates are connected with the wires D and E by means of the copper plates L and K attached to the ends of the wooden trough in which the cells are arranged. The wire D (fig. 16), which is connected with the last *zinc* plate of the battery, is often called the "*negative* pole;" whilst E, in connexion with the last *platinum* plate, is called the "*positive* pole."

Fig. 18.

When the connexion is established by means of the wires D and E with the "decomposing cell" (A), the "galvanic current" is commonly said to pass along the wire E to the platinum plate C, through the acidulated water in the decomposing cell, to the platinum plate B, and thence along the wire D back to the battery.

22. During this "passage of the current" (which is only a figurative mode of expressing the transfer of the electric influence), the water intervening between the plates B and C is decomposed, its hydrogen being attracted to the plate B (negative pole), and the oxygen to the plate C (positive pole). The gases can be seen adhering in minute bubbles to the surface of each plate, and as they increase in size they detach themselves, rising through the acidulated water in the tubes H and O, in which the two gases are collected.

Since no transmission of gas is observed between the two plates, it is evident that the H and O separated at any given moment from each plate do not result from the decomposition of one particle of water, but from two particles, as represented in fig. 19, where A represents the particles of *water lying between* the plates P and Z before the "current" is passed,

ıe state of the particles when the current has been established.
: positive pole) in connexion with the last platinum plate of the
and Z is (the negative pole) in connexion with the last zinc

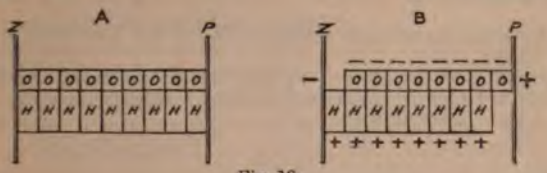


Fig. 19.

ıs + and − made use of in B refer to a common mode of account-
he decomposition of water by the battery, on the supposition that
ɣen is in a negatively electric condition, and therefore attracted by
tive pole P; whilst the hydrogen is in a positively electric condi-
d is attracted by the negative pole Z.

lecomposition of compounds by galvanic electricity is termed *elec-*

* When a compound of a metal with a non-metal is decomposed
manner, the metal is usually attracted to the (negative) pole in
ɔn with the zinc plate of the battery, whilst the non-metal is
l to the (positive) pole connected with the platinum plate of the

e the metals are frequently spoken of as *electro-positive* elements,
non-metals as *electro-negative*.

f the passage of the "current" be interrupted when the tube H has
full of gas, the tube O will be only half full, since *water contains*
n and oxygen in the proportion of two volumes of hydrogen to one
of oxygen. When the wider portions of the tubes (fig. 16) are
d, the two gases may be distinguished by opening the stop-cocks
ssion, and presenting a burning match. The hydrogen will be
ɔy its kindling with a slight detonation, and burning with a very
ne at the jet; whilst the oxygen will very much increase the bril-
f the burning match, and if a spark left at the extremity of the
e presented to the oxygen, the spark will be kindled into a flame.
ɣen will be found to smell strongly of ozone, and will impart a
ıe tinge to the iodised starch paper (see *Ozone*).

ıer method of effecting the decomposition of water by electricity
in passing a succession of electric sparks through steam. It is
: that in this case the decomposition is produced rather by the
heat of the spark than by its electric influence.†

his purpose, however, the galvanic battery does not suffice, since
t can be passed through any appreciable interval between the wires
ɔattery, a fact which electricians refer to in the statement that
ı the *quantity* of electricity developed by the galvanic battery is
s *intensity* is too low to allow it to discharge itself in sparks like
tricity from the machine or from the induction-coil, which pos-
very high intensity, though its quantity is small.

The most convenient instrument for producing a succession of elec-

:ɛρον (amber—root of *electricity*); λύω, to loosen.

† a very intense heat is capable of decomposing water into its elements has long
wn. When globules of melted platinum are dropped into water, bubbles of
and oxygen are disengaged.

tric sparks is the *induction-coil*, by the aid of which the electric influence of even a single cell of the galvanic battery may be so accumulated as to become capable of discharging itself in sparks, such as are obtained from the electrical machine.*

Fig. 20 represents the arrangement for exhibiting the decomposition of steam by the electric spark.

A is a half-pint flask furnished with a cork in which three holes are bored; in one of these is inserted the bent glass tube B, which dips beneath the surface of the water in the trough C.

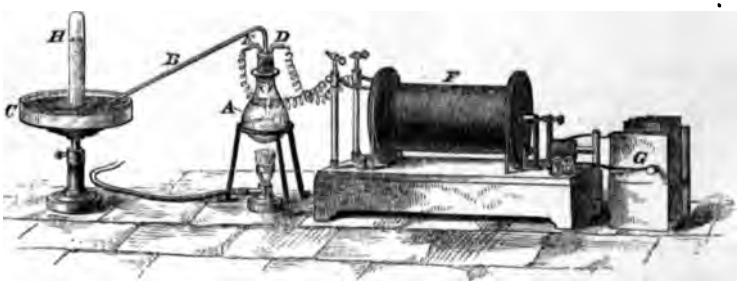


Fig. 20.--Decomposition of steam by electric sparks.

D and E are glass tubes, in each of which a platinum wire has been sealed so as to project about an inch at both ends of the tube. These tubes are thrust through the holes in the cork, and the wires projecting inside the flask are made to approach to within about $\frac{1}{16}$ inch, so that the spark may pass easily between them.

The flask is somewhat more than half filled with water, the cork inserted, and the tube B allowed to dip beneath the water in the trough; the wires in D and E being connected with the thin copper wires passing from the induction-coil F, which is connected by stout copper wires with the small battery G.

The water in the flask is boiled for about fifteen minutes, until all the air contained in the flask has been displaced by steam. When this is the case, it will be found that if a glass test-tube (H) filled with water be inverted† over the orifice of the tube B, the bubbles of steam will entirely condense, with the usual sharp rattling sound, and only insignificant bubbles of air will rise to the top of the test-tube. If now, whilst the boiling is still continued, the handle of the coil (F) be turned so as to cause a succession of sparks to pass through the steam in the flask, large bubbles of incondensable gas will accumulate in the tube H. This gas consists of the hydrogen and oxygen gases in a *mixed* state, having been released from their *combined* condition in water by the action of the electric sparks. The gas may be tested by closing the mouth of the tube H with the thumb, raising it to an upright position, and applying a lighted match, when a sharp detonation will indicate the recombination of the gases.‡

25. In the preceding experiments, the force of chemical attraction holding the particles of oxygen and hydrogen together in the form of water, has been overcome by the physical forces of heat and electricity. But water may be more easily decomposed by acting upon it with some element which has a sufficiently powerful chemical attraction for the oxygen of water to draw it away from the hydrogen.

* For a description of the induction-coil, see Miller's "Elements of Chemistry," Part I. p. 532.

† The end of the tube B should be bent upwards and thrust into a perforated cork with notches cut down the sides. By slipping this cork into the neck of the test-tube, the latter will be held firmly.

‡ With a powerful coil, a cubic inch of explosive gas may be collected in about fifteen *minutes*.

No non-metallic element is capable of abstracting the oxygen from water at the ordinary temperature.

Among the practically important metals, the five which have been mentioned as undergoing oxidation in dry air at the ordinary temperature, effect the immediate decomposition of water.

Metals which decompose water at the ordinary temperature.—Potassium, Sodium, Barium, Strontium, Calcium.

When a piece of potassium is thrown upon water it takes fire and burns with a fine violet flame, floating about as a melted globule upon the surface of the water, combining with the oxygen, and producing, in the act of combination, enough heat to kindle the hydrogen as it escapes. The violet colour of the flame is due to the presence of a little potassium in the form of vapour. The water will be found to change red litmus paper to blue, from the presence of the alkali potash (KO) formed by the combination of the potassium with the oxygen. The decomposition of the water is expressed by the equation

$$\underset{\text{Water.}}{HO} + K = \underset{\text{Potash.}}{KO} + H$$

from which we learn that one combining weight (39 parts) of potassium has been substituted for one combining weight (1 part) of hydrogen. 39 parts by weight of potassium, therefore, have the same power as 1 part of hydrogen, to combine with 8 parts (one combining weight) of oxygen. It is found that whenever potassium takes the place of hydrogen in a compound, 39 parts of the former are exchanged for one of the latter, and this is generally expressed by stating that 39 is the *chemical equivalent* of potassium.

(DEF.—The *chemical equivalent of a metal* expresses the weight which is required to be substituted for one part by weight of hydrogen in its compounds.)

The action of potassium upon water is an example of the production of compounds by substitution of one element for another, a mode of formation which is far more common than the production of compounds by direct combination of their elements.

Sodium has a less powerful attraction for oxygen than potassium, and does not usually take fire when thrown into cold water, although it is at once fused by the heat evolved in its combination with the oxygen. By holding a lighted match over the globule as it swims upon the water, the hydrogen may be kindled, when its flame is bright yellow from the presence of the sodium. The solution will be found strongly alkaline from the soda produced. By placing the sodium on a piece of blotting paper laid on the water, it may be made to ignite the hydrogen spontaneously, because the paper keeps it stationary, and prevents it from being so rapidly cooled by the water. Several cubic inches of hydrogen may easily be collected by placing a piece of sodium as large as a bean *in a small wire-gauze box (A, fig. 21)*, and holding it under an inverted

Fig. 21.

cylinder (B) filled with water and standing upon a bee-hive shelf. The equation representing the action of sodium upon water,

$$\underset{\text{Water.}}{HO} + Na = \underset{\text{Soda.}}{NaO} + H$$

shows that one combining weight (23 parts) of sodium is substituted for one combining weight (1 part) of hydrogen, and, in accordance with the definition above given, 23 is the chemical equivalent of sodium.

Barium, strontium, and calcium decompose water less rapidly than potassium and sodium; the results of their action upon water are, respectively, baryta (BaO), strontia (SrO), and lime (CaO). These substances have strongly alkaline characters, but as they are far less soluble in water than potash and soda, they have been distinguished as *alkaline earths*.

The tendency of heat to produce the union of metals with oxygen being known, it might be expected that metals which refuse to decompose water at the ordinary temperature, would be induced to do so if the temperature were raised, and accordingly magnesium and manganese, which are without action upon cold water, decompose it *at the boiling point*, disengaging hydrogen, and producing magnesia (MgO, a feebly alkaline earth) and oxide of manganese (MnO).

But the greater number of the common metals must be raised to a much higher temperature than this in order to enable them to decompose water. The following metals will abstract the oxygen from water at high temperatures, those at the commencement of the list requiring to be heated to redness (about 1000° F.), and the temperature required progressively increasing, until it attains whiteness for those at the end of the list.

Metals which decompose water at a temperature above a red heat.—Zinc, Iron, Chromium, Cobalt, Nickel, Tin, Antimony, Aluminum, Lead, Bismuth, Copper.

The *noble metals*, as they are called, which exhibit no tendency to oxidise in air, are incapable of removing the oxygen from water, even at high temperatures.

Metals which are incapable of decomposing water.—Mercury, Silver, Gold, Platinum.

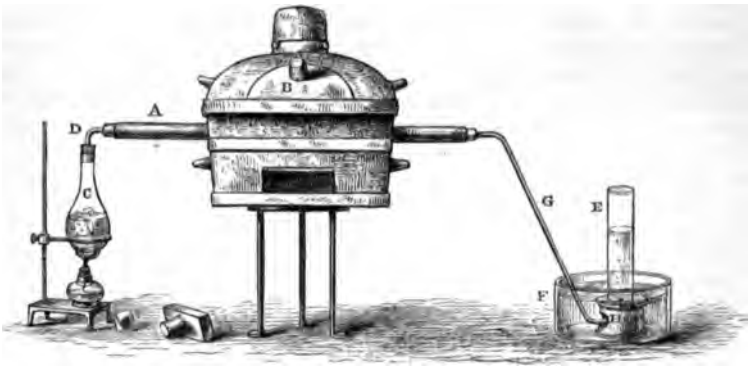


Fig. 22.—Preparation of hydrogen from steam.

26. *Preparation of hydrogen.*—The simplest process, chemically speaking, for preparing hydrogen in quantity, consists in passing steam *over red-hot iron.* An iron tube (A, fig. 22) is filled with iron nails and

fixed across a furnace (B), in which it is heated to redness by a charcoal fire. A current of steam is then passed through it by boiling the water in the flask (C), which is connected with the iron tube by a glass tube (D) and perforated corks. The hydrogen is collected from the glass tube (G) in cylinders (E) filled with water, and inverted in the trough (F) upon the bee-hive shelf (H), the first portions being allowed to escape, as containing the air in the apparatus. The iron combines with the oxygen of the water to form the black oxide of iron (Fe_3O_4), which will be found in a crystalline state upon the surface of the metal. The decomposition is represented by the equation

$$\underset{\text{Water.}}{4HO} + Fe_3 = \underset{\text{Black oxide of iron.}}{Fe_3O_4} + H_4$$

from which it would appear that three combining weights ($28 \times 3 = 84$ parts) of iron are substituted for four combining weights (4 parts) of hydrogen; and according to the definition given above, the chemical equivalent of iron should be expressed by 21, that being the weight required to be substituted for 1 part of hydrogen. Since, however, this is found to be the only case in which iron displaces hydrogen in this proportion, it is better to represent the action of water upon red-hot iron as taking place in two successive stages, of which the first is represented by the equation

$$\underset{\text{Water.}}{HO} + Fe = \underset{\text{Ferrous oxide.}}{FeO} + H$$

and the second by

$$HO + \underset{\text{Ferrous oxide.}}{3\,FeO} = \underset{\text{Black oxide of iron.}}{Fe_3O_4} + H^*$$

According to the first of these equations, one combining weight (28 parts) of iron is substituted for one combining weight of hydrogen, and, accordingly, 28 would represent the chemical equivalent of iron.

The process by which hydrogen is most commonly prepared depends upon the circumstance, that many of those metals which are able to decompose water, either at ordinary or elevated temperatures, will also decompose it in the presence of an acid without the assistance of heat.

Metals which decompose water at the ordinary temperature in the presence of an acid.—Potassium, Sodium, Barium, Strontium, Calcium, Magnesium, Manganese, Zinc, Iron, Chromium, Cobalt, Nickel.

Zinc is the most convenient metal to employ for the preparation of hydrogen in this way. It is used either in small fragments or cuttings, or as *granulated zinc*, prepared by melting it in a ladle and pouring it from a height of three or four feet into a pailful of water. The zinc is placed in the bottle (A, fig. 23), covered with water to the depth of two

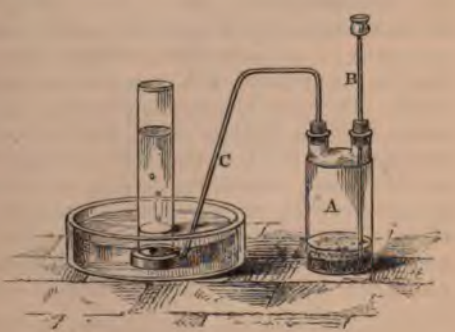


Fig. 23.—Preparation of hydrogen.

* This view is supported by the fact that FeO (protoxide of iron), when prepared by other processes, is capable of decomposing water in accordance with the second equation.

or three inches, and diluted sulphuric acid slowly poured in through the funnel tube (B) until a pretty brisk effervescence is observed. The hydrogen is unable to escape through the funnel tube, since the end of it is beneath the surface of the water, but it passes off through the bent tube (C), and is collected over water as usual, the first portions being rejected as containing air. The chemical change is expressed in the equation

$$\underset{\text{Sulphuric acid combined with water.}}{HO\,.\,SO_3} + Zn = \underset{\text{Sulphate of zinc.}}{ZnO\,.\,SO_3} + H$$

from which it appears that one combining weight (32·8 parts) of zinc is substituted for one combining weight (1) of hydrogen, and that 32·8 represents the chemical equivalent of zinc.*

By evaporating the larger excess of water from the solution left in the bottle, crystals of sulphate of zinc (*white vitriol*) may be obtained. It would not be possible to fulfil the above equation without adding a great deal more water than is there represented, in order to dissolve the sulphate of zinc.

It will be noticed that the liquid becomes very hot during the action of the acid upon the zinc, the heat being produced by the combination which is taking place. The black flakes which separate during the solution of the zinc consist of metallic lead, which is always present in the zinc of commerce, and much accelerates the evolution of hydrogen by causing galvanic action. Pure zinc placed in contact with diluted sulphuric acid evolves hydrogen very slowly.

Iron might be used instead of zinc, and the solution when evaporated would then deposit crystals of *green vitriol* or *copperas* (sulphate of iron $FeO\,.\,SO_3$), the action of iron upon water in the presence of sulphuric acid being represented by the equation

$$\underset{\text{Sulphuric acid combined with water.}}{HO\,.\,SO_3} + Fe = \underset{\text{Sulphate of iron.}}{FeO\,.\,SO_3} + H$$

which shows that one combining weight (28) of iron has taken the place of one combining weight of hydrogen. 28 would then be the chemical equivalent of iron.

27. *Physical properties of hydrogen.*—This gas is permanent, invisible, and inodorous when pure. The hydrogen obtained by the ordinary methods has a very disagreeable smell, caused by the presence of minute quantities of compounds of hydrogen with sulphur, arsenic, and carbon; but the gas prepared with pure zinc and sulphuric acid is quite free from smell. The most remarkable physical property of hydrogen is its lightness. It is the lightest of all kinds of matter. The specific gravity of hydrogen is 0·0692, so that it is about $\frac{1}{15}$ as heavy as air. This lightness would strongly recommend hydrogen as the unit of comparison for the specific gravities of gases, and theoretical considerations would compel the admission of an elementary standard in place of a somewhat variable mixture like atmospheric air. But since the hydrogen required to fill a pint globe weighs only three quarters of a grain, whilst the same volume

* Many explanations have been offered to account for the circumstance that the Zn will decompose HO in the presence of SO_3, although this latter has no attraction for either of the elements of the HO. One of the most satisfactory appears to be that which refers the decomposition to the attraction of the Zn for the group represented by $[OSO_3]$, which is *greater than the attraction* of H for the same group, whilst the attraction of H for O alone, *at the ordinary temperature*, is greater than that of Zn for O.

of air weighs ten grains and three quarters, it will be seen that no balance of even considerable accuracy could be depended upon for the practical determination of the specific gravities of gases if hydrogen were the standard employed.

In calculating the weights and volumes of gases, it will be found of great service to remember that *one grain of hydrogen measures* 46·73 *cub. in. at* 60° *F. and* 30 *in. Bar.*

The lightness of hydrogen may be demonstrated by many interesting experiments. Soap bubbles or small balloons (of *collodion* for example) will ascend very rapidly if inflated with hydrogen. A light beaker glass may be accurately weighed in a pair of scales; it may then be held with its mouth downwards, and hydrogen poured up into it from another vessel. If it be then replaced upon the scale-pan with its mouth downwards, it will be found very much lighter than before. Another form of the experiment is represented in fig. 24, where a light glass shade has been suspended from the balance and counterpoised, the equilibrium being, of course, at once

Fig. 24.

disturbed when hydrogen is poured up into the shade. If a jar full of hydrogen be held with its mouth downwards, and a piece of smouldering brown paper held under it, the smoke, which would rise freely in the air, is quite unable to rise through the hydrogen, and remains at the mouth of the jar.

28. It will be observed, in these experiments, that the gas gradually *falls* out of the jar, notwithstanding its lightness, and is replaced by air. This is accounted for by a physical property belonging to all gases (and vapours) called *diffusibility*, which may be defined as *the tendency of the particles of a gas to separate as far as possible from each other.* If a jar of hydrogen were placed with its mouth downwards over a jar of air, this mutual repulsion among the particles of each gas would cause it to *diffuse* itself equally throughout both jars, so that, eventually, as much hydrogen would be found in the lower jar as if it had been completely exhausted of air before the commencement of the experiment. This is often expressed by the statement that *one gas acts as a vacuum to another*, which is true as far as the ultimate result is concerned, though, of course, the time occupied by the passage of a gas into a *vacuum* would be far less than *that required for its passage into another gas.* Even if the two jars be

connected only by a tube with the narrowest passage possible, the same result would be arrived at, but after a longer period. If the two gases were separated by a plate of some material having no visible passages, such as paper, or plaster of Paris, a complete interchange would still take place, and after a time each gas would be found equally distributed through both jars. By thus interposing a porous obstacle so as to retard the diffusion of the gas, the rapidity with which the particles of gases separate from each other in consequence of this mutual repulsion may be ascertained. The *diffusion tube* (fig. 25) employed for this purpose is a glass tube (A) closed at one end by a plate of plaster of Paris (B). If this tube be filled with hydrogen,* and its open end immersed in coloured water, the water will be observed to rise rapidly in the tube, on account of the rapid escape of the hydrogen through the pores of the plaster. The external air, of course, passes into the tube through the pores at the same time, but much less rapidly than the hydrogen passes out, so that the ascent of the column of water (C) marks the difference between the volume of hydrogen which passes out, and that of air which passes into the

Fig. 25.

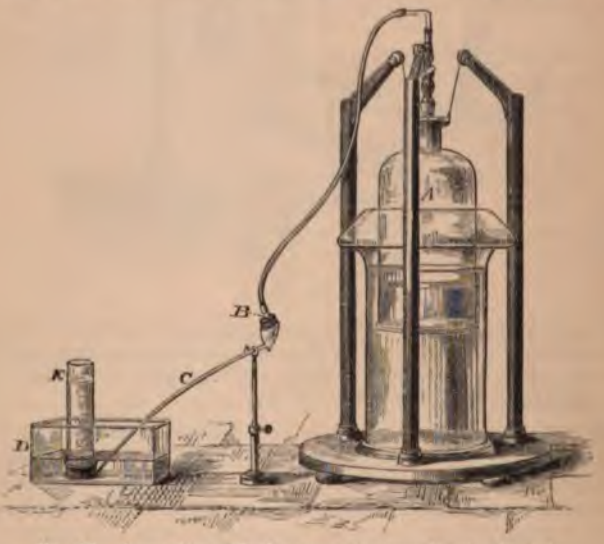


Fig. 26.—Separation of hydrogen and oxygen by atmolysis.†

tube in a given time, and allows a measurement to be made of the *rate of diffusion*; that is, of the velocity with which the gas issues on account of the repulsion among its particles, as compared with the velocity with

* This tube must be filled by displacement (see fig. 30), in order not to wet the plaster. A piece of sheet caoutchouc may be tied over the plaster of Paris, so that diffusion may not commence until it is removed.

† *This term has* been applied to the separation of gases by diffusion; *ἀτμός, vapour—λύω, to loosen.*

air enters, this velocity being always taken as unity.* To deter-
rate of diffusion, it is of course necessary to maintain the water
ne level within and without the diffusion tube, so as to exclude
nce of pressure.

ment has established the law that
of diffusion of gases are inversely
are roots of their specific gravi-
example, the specific gravities of
nd hydrogen stand to each other
tio of 16 : 1; the ratio of their
ots will therefore be 4 : 1, and
s of diffusion will be in the in-
io, or 1 : 4; that is, hydrogen
ape through minute openings with
es the velocity of oxygen; and
y experience shows that a cracked
bottle with a badly fitting stop-
often be used to retain oxygen,
hydrogen. Again, the specific
of air and hydrogen, being respec-
and ·069, their rates of diffusion
and $\frac{1}{\sqrt{\cdot 069}}$ or 3·8, so that in the
nt with the diffusion tube, 3·8
hes of hydrogen would pass out,
cubic inch of air passed in; and
fluence of pressure be excluded,
inches of water would enter the

Fig. 27.

at difference in the rates of diffusion
en and oxygen may be easily shown
angement represented in fig. 26. A
led with a mixture of two volumes of
th one volume of hydrogen, communi-
ough the stop-cock and flexible tube
glass tube B, which is fitted through
ed cork in the bowl of the common
pe C, the sealing-waxed end of which
water in the trough D. By opening
ck and pressing the jar down in the water, the mixed gases may be forced
rough the pipe, and if a small cylinder (E) be filled with them, the mixture
nd to detonate violently on the approach of a flame. But if the gas be
pass very slowly through the pipe (at the rate of about a cubic inch per
he hydrogen will diffuse through the pores of the pipe so much faster than
n, that the gas collected in the cylinder will contain so little hydrogen as
nger explosive, and to exhibit the property of oxygen to rekindle a partly
ed match.†

very striking illustration of the high rate of diffusion of hydrogen is
as represented in fig. 27. A is a cylinder of porous earthenware (such as

ing a mixture of nitrogen and oxygen, its rate of diffusion is intermediate between
those gases; however, since the proportions of the gases are very nearly con-
rror of any magnitude arises.
houc and varnished silk, being impervious to air, do not permit ordinary diffu-
e place through them. Yet they are capable of transmitting gases by a peculiar
tion, which may be compared to their power of transmitting ether and other
able of wetting them. In this manner oxygen has been found to be transmitted
y than nitrogen, so that by placing atmospheric air in contact with a film of

are employed in galvanic batteries) closed at one end, and furnished at the other with a perforated bung, through which passes a glass tube B, about three feet long, and half an inch in diameter. The bung is made air-tight by coating it with sealing wax dissolved in spirit of wine. This tube being supported so that its lower end dips about an inch below the surface of water, a jar of hydrogen is held over the porous cylinder, when the self-repulsion of the particles of the gas is manifested by their being forced (not only out of the mouth of the jar C, which is open at the bottom, but also) through the pores of the earthenware jar, the air from which is violently driven out, as if by blowing, through the tube, and is seen bubbling up rapidly through the water. When the air has ceased to bubble out, and a large volume of hydrogen has entered the porous jar, the bell-jar C is removed, when the hydrogen escapes so rapidly through the pores, that a column of twenty or thirty inches of water is drawn rapidly up the tube B. If the greatest height to which the water ascends be marked, and when it has returned to its former level, a jar of coal-gas be held over the porous cylinder, it will be found that the above phenomena are manifested in a much lower degree, showing that coal-gas, being heavier than hydrogen, does not pass nearly so rapidly through the pores of the earthenware as hydrogen does.

Fig. 28.

29. *Chemical properties of hydrogen.* — The most conspicuous chemical property of hydrogen is its disposition to burn in air when raised to a moderately high temperature, entering into combination with the oxygen of the air to form water. The formation of water during the combustion of hydrogen gave rise to its name (ὑδωρ, water).

On introducing a taper into an inverted jar of hydrogen (fig. 28), the flame of the taper will be extinguished, but the hydrogen will burn with a pale flame at the mouth of the jar, and the taper may be rekindled at its flame by slowly withdrawing it.

The lightness and combustibility of hydrogen may be illustrated simultaneously by some interesting experiments. If two equal gas cylinders be filled with hydrogen, and held with their mouths respectively upwards and downwards, it will be

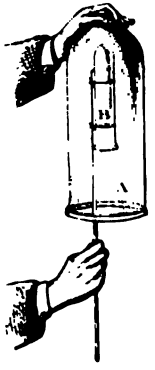


Fig. 29.

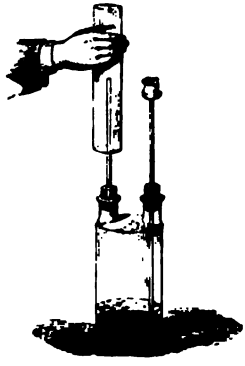


Fig. 30.

caoutchouc, on the other side of which a vacuum is maintained, a gaseous mixture may be made to pass through the film, containing 41·6 per cent. by volume of oxygen, instead of 21 per cent., usually present in air. Such a mixture, of course, accelerates combustion in a very high degree. It appears to be in consequence of a similar action that hydrogen is capable of passing through red-hot platinum and iron tubes.—(Graham, *Proc. Roy. Soc. June 1866.*)

found, on testing each with a taper after the same interval, that the hydrogen has entirely escaped from the cylinder held with its mouth upwards, whilst the other still remains nearly filled with the gas.

The hydrogen may be scooped out of the jar A (fig. 29) with the small cylinder B attached to a handle. On removing B, and applying a taper to it, the gas will take fire.

A cylinder may be filled with hydrogen by displacement of air (fig. 30), if the tube from the hydrogen bottle be passed up into it.

If such a dry cylinder of hydrogen be kindled whilst held with its mouth downwards, the formation of water during the combustion of the hydrogen will be indicated by the deposition of dew upon the sides of the cylinder.

By softening a piece of glass tube in the flame of a spirit-lamp, drawing it out, and filing it across in the narrowest part (fig. 31), a jet can be made from which the hydrogen may be burnt. This jet may be fitted by a perforated cork to any common bottle for containing the zinc and sulphuric acid (fig. 32).

Fig. 31.

The hydrogen must be allowed to escape for some minutes before applying a light, because it forms an explosive mixture with the air contained in the bottle. This may be proved, without risk, by placing a little granulated zinc in a soda-water bottle, pouring upon it some diluted sulphuric acid, and quickly inserting a perforated cork, carrying a piece of glass tube about three inches long, and one-eighth of an inch wide. If this tube be immediately applied to a flame, the mixture of air and hydrogen will explode, and the cork and tube will be projected to a considerable distance.

By inverting a small test-tube over the jet in fig. 32, a specimen of the hydrogen may be collected, and may be kindled, to see if it burns quietly, before lighting the jet.

A dry glass, held over the flame, will collect a considerable quantity of water, formed by the combustion of the hydrogen.

Fig. 32.

The combustion of hydrogen produces a greater heating effect than that of an equal weight of any other combustible body. It has been determined that 1 gr. of hydrogen, in the act of combining with 8 grs. of oxygen, produces enough heat to raise 62,031 grs. of water from 32° F. to 33° F. (or 34,462 grs. from 0° C. to 1° C.)

The temperature of the hydrogen flame has been estimated at 5898° F., which is higher than that of any other single flame with which we are acquainted.

Notwithstanding its high temperature, the flame of hydrogen is almost devoid of illuminating power, on account of the absence of solid particles.

30. If a taper be held several inches above a cylinder of hydrogen, standing with its mouth upwards, the gas will be kindled with a loud explosion, because an explosive mixture of hydrogen and air is formed in and around the mouth of the cylinder.

Fig. 33.

If a stoppered gas jar (fig. 33) be filled with hydrogen, and supported upon three blocks, it will be *found, if the hydrogen be kindled at the* neck of the jar, that it will burn

quietly until air has entered from below in sufficient proportion to form an explosive mixture, which will then explode with a loud report.

The same experiment may be tried on a smaller scale, with the two-necked copper vessel (fig. 34), the lower aperture being opened some few seconds after the hydrogen has been kindled at the upper one.

Fig. 34.

The explosion of the mixture of hydrogen and air is due to the sudden expansion caused by the heat generated in the combination of the hydrogen with the oxygen throughout the mixture. After the explosion of the mixture of hydrogen and air (oxygen and nitrogen), the substances present are steam (resulting from the combination of the hydrogen and oxygen) and nitrogen, which are expanded by the heat developed in the combination to a volume far greater than the vessel can contain, so that a portion of it issues very suddenly into the air around, the collision with which produces the report.

If pure oxygen be substituted for air, the explosion will be more violent, because the mixture is not diluted with the inactive nitrogen. The calculated pressure exerted by the mixture of hydrogen and oxygen, when exploded, amounts to 26 atmospheres, or 390 lbs. upon the square inch, whilst the mixture of hydrogen and air is calculated to exert a pressure of 12·5 atmospheres, or 187 lbs. per inch.

The experiment may be made safely in a soda-water bottle. The bottle is filled with water, and inverted with its mouth beneath the surface of the water; enough oxygen is then passed up into it to fill one-third of its volume; if the remainder of the water be then displaced by hydrogen, and the mouth of the bottle be presented to the flame of a spirit-lamp, a very violent explosion will result, attended with a vivid blue flash in the bottle. If the mouth of the bottle be presented towards a disc of paper, previously suspended at a distance of 20 or 30 inches, the paper will be violently torn to pieces, bearing witness to the concussion between the expanded steam issuing from the bottle and the external air.

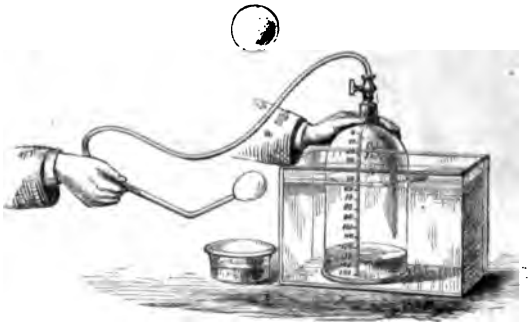


Fig. 35.

If some of the mixture be introduced into a capped jar, provided with a piece of caoutchouc tubing, and a small glass tube, and pressed down in a trough of water, soap-bubbles may be inflated with it, which will ascend rapidly in the air, and explode *violently* when touched with a flame (fig. 36).

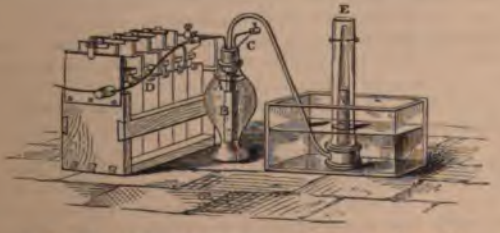
In order to demonstrate the production of water in the explosion, the *Cavendiometer** (fig. 36) is employed. This is a glass vessel, with a stopper firmly secured by cap (A), and provided with two platinum wires which pass through the stopper, and approach near to each other within the eudiometer, so the electric spark may easily be passed between By screwing the stop-cock B into the plate of air-pump, the eudiometer may be exhausted. It is screwed on to the jar represented in fig. 37, contains a mixture of two measures of hydrogen with one measure of oxygen, standing over On opening the stop-cocks between the two the eudiometer becomes filled with the mixand the quantity which has entered is indicated rise of the water in the jar. The glass stop-C having been closed, to prevent the brass cap being forced off by the explosion, the eudiois again screwed on to its foot, and an electric passed between the platinum wires, either a Leyden jar or an induction coil, when the two gases will combine with a flash of light, attended with a very slight concussion, since there is no col-

Fig. 36.

with the external air. For an instant a is perceived within the eudiometer, which nses into fine drops of dew, consisting of water formed by the combination of the which was here induced by the high temure of the electric spark, as it was in the r experiment by the high temperature of flame. If the gases have been mixed in tact proportion of two measures of hydrogen measure of oxygen, the eudiometer will e again vacuous, and if it be screwed on to pped jar, may be filled a second time with ixture, which may be exploded in the same er.

Fig. 37.

e entire disappearance of the gases may be red obvious to the eye by exploding the re over mercury. For this purpose the gases should be collected from water itself, is strongly acidified with sulphuric acid, decomposed in the *voltameter* (A, fig. 38) e aid of five or six cells of Grove's battery. The voltameter contains two um plates (B), attached to the platinum wires C and D, which are connected the opposite poles of the battery. The first few bubbles of the mixture of gen and oxygen evolved having been allowed to escape, in order to displace the



Fig, 38.—Detonating gas collected from voltameter.

o named from εὖδιος, fine or clear, and μέτρον, a measure, because an instrument the same principle has been used to determine the degree of purity of the atmosphere. articular form of eudiometer here described was employed by Cavendish about the *1770, for the synthesis of water.*

air, the gas may be collected in the small eudiometer (E), which has been previously filled with water. This eudiometer is a cylinder of very thick glass,* closed at one end, and having two stout platinum wires cemented into holes drilled near the closed end, the wires approaching sufficiently near to each other to allow the passage of the electric spark. Having been filled with the mixture of hydrogen and oxygen from the voltameter, the eudiometer is closed with the finger, and transferred to a basin containing mercury, where it is pressed firmly down upon a stout cushion of india-rubber, and the spark passed through the mixed gases, either from the coil or the Leyden jar. The combustion takes place with violent concussion, but without noise; and since the eudiometer is vacuous after the gases have combined, the cushion will be found to be very firmly pressed against its open end. On loosening the cushion, the mercury will be violently forced up into the eudiometer, which will be completely filled with it, proving that when an electric spark is passed through the mixture of two volumes of hydrogen and one volume of oxygen, no residue of gas remains.†

32. The knowledge of the volumes in which hydrogen and oxygen combine, is turned to account in the analysis of gases, to ascertain the proportion of hydrogen or oxygen contained in them. Suppose, for example, it be required to determine the amount of oxygen in a sample of atmospheric air, the latter is mixed with hydrogen, in more than sufficient quantity to combine with the largest proportion of oxygen which could be present, and when the combination has been induced by the electric spark, the volume of gas which has disappeared (2 vols. H + 1 vol. O) has only to be divided by three to give the volume of the oxygen.

A bent eudiometer (fig. 89) is generally employed for this purpose. Having been completely filled with water, it is inverted in the trough, and the specimen of air is introduced (say 0·5 cubic inch). The open limb is then closed by the thumb, and the eudiometer turned so as to transfer the air to the closed limb. A stout glass rod is thrust down the open limb, so as to displace enough water to equalise the level in both limbs, in order that the volume of the air may not be diminished by the pressure of a higher column of water in the open limb. The volume of the included air having been accurately noted, the open limb of the tube is again filled up with water, inverted in the trough, and a quantity of hydrogen introduced, equal to about half the volume of the air. This having been transferred, as before, to the closed limb, the columns of water are again equalised, and the volume of the mixture of air and hydrogen ascertained. The open limb is now firmly closed with the thumb, and the electric spark passed through the mixture, either from the Leyden jar or the induction coil. On removing the thumb, after the explosion, the volume of gas in the closed limb will be found to have diminished very considerably. Enough water is poured into the open limb to equalise the level, and the volume of gas is observed. If this volume be subtracted from the volume before explosion, the volume of gas which has disappeared will be ascertained, and one-third of this will represent the oxygen, which has condensed with twice its volume of hydrogen into the form of water. Thus the numbers recorded will be—

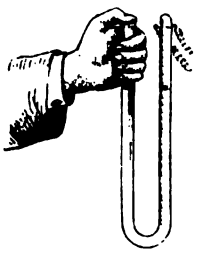


Fig. 39.
Siphon eudiometer.

* The bore of this eudiometer should be about half an inch in diameter, and the thickness of its sides about three-eighths of an inch; its length is 7 inches.

† This fact may also be demonstrated with the siphon eudiometer, shown in fig. 39, by confining about a cubic inch of the explosive mixture in the closed limb, over water, and stopping the open limb securely with a cork, so as to leave a space filled with air between the cork and the water. The eudiometer must be very firmly fixed on a stand, or it will be broken by the concussion. After it has been proved, it may be held in the hand, as in the figure. By firing mixtures of hydrogen and oxygen, in different proportions, in the same manner, it may be shown that any excess of either gas above the ratio of 2H : 1O will *remain uncombined* after the explosion.

Volume of air analysed,	0·50 cub. in.
Volume of air mixed with hydrogen,	0·75 ,,
After explosion,	0·45 ,,
Difference, (⅓ H and ⅓ O)	·30 ,,

·30, divided by 3 = ·10 cub. in. of oxygen.

It is evident that the volume of hydrogen contained in a gas might be ertained in a similar manner, by exploding with oxygen, and taking -thirds of the gas which had disappeared in the form of water to re-sent the volume of hydrogen.

In exact experiments, a correction would be required for any variation the temperature or barometric pressure during the progress of the lysis.

33. It will have been observed, in the experiment upon the synthesis water in the Cavendish eudiometer, that the volume of water obtained very small in comparison with that of the gases before combination. t it is evident that no comparison can, with propriety, be made between volume of a compound, in the liquid or solid state, and that of its nponents in the gaseous state, since the particles of the former are der the influence of the cohesive force from which those of the latter free. For the purposes of such a comparison the volume of the com-nd body must be taken under precisely the same physical conditions the volume of its components.

If the mixture of hydrogen and oxygen be measured and exploded at emperature above the boiling point of water, it is found that the steam duced occupies two-thirds of the volume of the mixed gases, measured the same temperature and atmospheric pressure. Hence, *two volumes hydrogen combine with one volume of oxygen to form two volumes of ueous vapour, at the same temperature and pressure.*

It very frequently happens, as in this instance, that the volume of a npound gas or vapour is less than the sum of the volumes of its con-tuent gases.

The relative volumes in which the gases unite could, of course, be in-red from a knowledge of their specific gravities and their combining ights. For since oxygen (sp. gr. 1·1057) is sixteen times as heavy as drogen (sp. gr. ·0692), equal volumes would give us sixteen parts by ight of the former to one of the latter gas; and we must take twice e volume of hydrogen in order to obtain the ratio of their combining ights (8 : 1).

The specific gravity of the vapour of water can also be calculated from e above data. Thus—

Specific gravity (or weight of one volume) of hydrogen,	·0692
Weight of two volumes of hydrogen,	0·1384
Specific gravity or weight of one volume of oxygen,	1·1057
Weight of two volumes of the vapour of water,	1·2441

Dividing this by two, we obtain for the

Weight of one volume, or specific gravity, of vapour of water,	0·622

ich agrees *with that obtained by actual* weighing.

34. The *combining volumes of gases and vapours* represent the relative volumes occupied by their combining weights. Hence, if one part by weight of hydrogen be represented as occupying one volume, eight parts (the combining weight) of oxygen must be represented as occupying half a volume. In order to avoid the fraction, however, the eight parts of oxygen may be represented as occupying one volume, so that the one part of hydrogen will correspond to two volumes, and the statement will be—

Combining volume of Oxygen = 1
" " Hydrogen = 2

35. *Atomic theory.*—In seeking for some explanation of the fact that the relative proportions by weight and volume in which the elements unite are fixed and definite, it occurred to Dalton that these elements are really composed of a collection of indivisible particles or *atoms** which possess a fixed weight for each element. Thus, if the weight of each atom of hydrogen be taken as = 1, and that of an atom of oxygen as = 8, it would follow, as a matter of course, that these elements must combine with each other, and with the other elements, in proportions represented by these numbers, or by some simple multiples of them, since *fractions* of *atoms* would be inconceivable.

This theory receives very great support from the fact which has been elicited by experiment, that the combining weights of all the elements which have been examined in the state of vapour or gas occupy the same volume as one part by weight of hydrogen, with the exception of oxygen, sulphur, selenium, phosphorus, arsenic, and tellurium, which occupy half that volume.

If, therefore, it be further assumed, that the atoms of the different elements, in the gaseous state, occupy equal volumes, the atomic theory will afford an adequate explanation of the laws of combination by weight and volume. But, upon this assumption, the numbers representing the *atomic weights* of oxygen and the other exceptions above mentioned would not be the same as their *combining weights* (which occupy only half a volume), but would be twice those weights.† Thus, the *atomic* weight of oxygen would be 16, since that number represents a weight of oxygen occupying the same volume as 1 part by weight of hydrogen, though its *equivalent* weight would be 8, which represents the weight of oxygen equal in chemical value to 1 part of hydrogen.

The formula representing the true atomic constitution of water therefore would be $H_2\Theta$ = 2 volumes of water, where H_2 represents 2 parts by weight, or two volumes, or two atoms of hydrogen, and Θ represents 16 parts, or one volume, or one atom of oxygen. A large number of modern chemists employ such formulæ, which represent the number of atoms (or volumes) of each element contained in the compound, in place of those expressing merely the number of combining weights or equivalents. The *atomic formulæ* are preferable in speculative chemistry for purposes of research, but the *equivalent formulæ* are more serviceable in the practical applications of chemistry, and will therefore be more generally adopted in these pages.

The belief in the existence of atoms is supported by the circumstance,

* Ἄτομος, indivisible.

† Since an *atom* ought to be the smallest conceivable particle of matter, there seems some *incongruity* in the idea of a combining weight or equivalent representing half the atomic *weight.*

that those weights of the elements which are assumed to represent the relative weights of their atoms require, in most cases, the same amount of heat to raise them through an equal number of degrees of temperature; in other words, the *atomic heats* of the elements, like their atomic volumes, are identical, whilst the amounts of heat required to raise *equal weights* (specific heats) of the elements through an equal number of degrees are expressed by very different numbers.

Thus, if the specific heat of water (or quantity of heat required to raise one part by weight of water through one degree) be represented by 1, that of oxygen is 0·2175, and that of hydrogen just sixteen times as great, or 3·409. Hence, it follows that a given weight of hydrogen in cooling down through a certain number of degrees, would give out 16 times as much heat as an equal weight of oxygen would give out, and that the atom (or one part by weight) of hydrogen is associated with the same amount of heat as the atom (or sixteen parts by weight) of oxygen; and since the specific heat represents the amount of heat associated with one part by weight of the element, the atomic heat of oxygen will be 16 times its specific heat ($0{\cdot}217 \times 16$), or 3·48, which coincides as nearly as can be expected with the atomic heat of hydrogen ($3{\cdot}409 \times 1$).

36. It has also been found that the combining weights of all compound substances which have been examined in the state of gas or vapour occupy either twice or four times the volume of one combining weight of oxygen.

Hence it appears that—

I. The *combining volume of an element* in the state of gas or vapour is either one volume (O, &c.), or two volumes (H, &c.).

II. The *combining volume of a compound* in the state of gas or vapour is either two volumes or four volumes.

The adoption of atomic formulæ (or *molecular* formulæ, see *binoxide of hydrogen*) in place of equivalent formulæ, is attended with great advantage in the study of the combining volumes of gases and vapours, since *the atomic symbol for an elementary substance represents one volume of its gas or vapour*, and *the molecular formula for a compound substance represents two volumes of its gas or vapour.*

37. The great energy with which hydrogen combines with oxygen is turned to account for the purpose of producing the highest temperature which can be obtained by any chemical process.

The *oxyhydrogen* blowpipe (fig. 40) is an apparatus for burning a jet of hydrogen mixed with half its volume of oxygen. The gases are supplied from separate gas-holders (or bags with pressure-boards and weights) through the tubes H and O, which conduct them into the brass sphere B. Each of these tubes is provided with a valve of oiled silk opening outwards, so as to prevent the passage of either gas into the receptacle containing the other. The tube A is stuffed with thin copper wires, which would rapidly conduct away the heat and extinguish the flame of the mixed gases burning at the jet, should it tend to pass back and ignite the mixture in B. The stop-cocks D and E allow the flow of the gases to be regulated so that they may mix in the right proportions. If the hydrogen be kindled first, it will be found that, as soon as the oxygen is turned on, the flame is reduced to a very much smaller volume, *because the undiluted oxygen* required to maintain it occu-

Fig. 40.—Oxyhydrogen blowpipe.

pies only one-fifth of the volume of the atmospheric air from which the hydrogen was at first supplied with oxygen. The heat developed by the combustion being therefore distributed over a much smaller area, the temperature at any given point of the flame must be much higher, and very few substances are capable of enduring it without fusion.* Lime is one of these; and if a cylinder of lime be supported, as at L, fig. 40, in the focus of the flame, its particles become heated to intense incandescence, and a light is obtained which is visible at night from very great distances, so as to be well adapted for signalling and lighthouses. For such purposes coal-gas is often used instead of hydrogen (*oxycalcium* light).

If a shallow cavity be scooped in a lump of quicklime, a few scraps of platinum placed in it, and exposed to the oxyhydrogen flame (fig. 41), a fused globule of platinum of very considerable size may be obtained in a few seconds. By employing a little furnace made of lime, Deville has succeeded in fusing platinum in quantities sufficient to cast large ingots, a result unattainable by any other furnace. Pipeclay, which resists the action of all ordinary furnace-heats, may be fused into a glass in this flame, whilst gold and silver are instantaneously melted, and vaporised into a dense smoke.

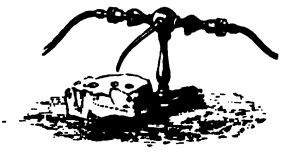


Fig. 41.

38. In its chemical relations to other elements, hydrogen is diametrically opposed to oxygen. Whereas the latter combines directly with the greater number of the elements, hydrogen will enter into direct combination with very few; *oxygen*, *chlorine*, *bromine*, *carbon*, *iodine*, and *sulphur* (the three last with difficulty), are the only elements which unite in a direct manner with hydrogen, and of these only chlorine and bromine combine with hydrogen at the ordinary temperature, though not without exposure to light. Again, whilst fluorine is not known to form any compound with oxygen, its combination with hydrogen (hydrofluoric acid) is one of the most stable compounds known, and it may be safely asserted that fluorine in the free state would combine with hydrogen even more readily than chlorine does. All the metals form compounds with oxygen, but very few combinations of metals with hydrogen have been obtained. Indeed, in its relations to other elements, hydrogen closely resembles the metals, though it does not fall within the definition of a metal given above, since it does not form a base with oxygen, and its combinations with the salt-radicals (chlorine, &c.) are acids, and not salts.

Water.

39. Pure water is not found in nature. Rain is the purest form of natural water, but contains certain gases which it collects from the atmosphere during its fall. As soon as it reaches the earth, it begins to dissolve small portions of the various solid materials with which it comes in contact, and thus becomes charged with salts and other substances to an extent varying, of course, with the nature of the soils and rocks which it has touched, and attaining its highest point in sea water, which contains a larger proportion of saline matters than water from any other natural source. Ice, when melted, affords nearly pure water, since, when water containing salts is partially frozen, these are left dissolved in the uncongealed water.

If a quantity of rain, spring, river, or sea water be boiled in a flask furnished with a tube also filled with the water, and passing under a gas cylinder standing in a trough of the same water (fig. 42), it will be found

* *The temperature of this flame has been estimated at above* 14,000° F.

to give off a quantity of gas which was previously held in solution by the water, and is now set free because *gases are less soluble in hot than in cold water*. The quantity of this gas will vary according to the source of the water, but it will always be found to contain the gases existing in atmospheric air, viz., nitrogen, oxygen, and carbonic acid. One gallon of rain water will generally furnish about 4 cubic inches of nitrogen, 2 cubic inches of oxygen, and 1 cubic inch of carbonic acid. It is worthy of remark, that the nitrogen and oxygen have been dissolved by the water, not in the proportions in which they exist in the atmosphere (4 N : 1 O), but in the proportions in which they ought to be dissolved, if it be true that they exist in the air in the condition of mere mechanical admixture. The oxygen thus carried down from the air by rain appears to be serviceable in maintaining the respiration of aquatic animals, and in conferring upon river waters a self-purifying power, by acting upon certain organic matters which would probably prove hurtful to animals, and converting them into harmless products of oxidation. In the cases of rivers contaminated with the sewage of towns, this action of the dissolved oxygen is probably of great importance. The carbonic acid dissolved in rain water also probably serves some useful purposes in the chemical economy of nature. (See *Carbonic Acid.*)

Fig. 42.

40. The waters of wells, springs, and rivers, and especially those of the two first-named sources, differ very much from each other, according to the nature of the layers of rock or earth over or through which they have passed, and from which they dissolve a great variety of substances, some of which are familiar to us in daily life, while others are only met with in chemical collections. Under the former head may be enumerated Glauber's salt (sulphate of soda), common salt (chloride of sodium), Epsom salt (sulphate of magnesia), gypsum (sulphate of lime), chalk (carbonate of lime), common magnesia (carbonate of magnesia), carbonic acid, and silica.

Among the substances known only to the chemist may be mentioned sulphuretted hydrogen, sulphate of potash, chloride of potassium, chloride of calcium, chloride of magnesium, phosphate of lime, bromides and iodides of calcium and magnesium (rarely), alumina (probably sulphate of alumina), carbonate of iron, and certain vegetable substances.*

The well waters of certain localities (as, for example, those of large towns) also frequently contain salts of nitric and nitrous acids, and of ammonia.

The waters of springs and rivers do not differ very materially from

* Although it is certainly known that the acids and bases capable of forming the salts here enumerated may be detected in spring and river waters, their exact distribution amongst *each other is still a matter of uncertainty.*

well waters as to the nature of the substances which they contain, though, in the case of river waters more particularly, the quantity of these substances is materially influenced by the conditions of rapid motion and exposure to air under which such waters are placed.

Household experience has established a classification of the waters from natural sources into *soft* and *hard* waters—a division which depends chiefly upon the manner in which they act upon soap. If a piece of soap be gently rubbed in soft water (rain water, for example) it speedily furnishes a froth or *lather*, and its cleansing powers can be readily brought into action; but if a hard water (spring water) be substituted for rain water, the soap must be rubbed for a much longer time before a lather can be produced, or its effect in cleansing rendered evident; a number of white curdy flakes also make their appearance in the hard water, which were not seen when soft water was used. The explanation of this difference is a purely chemical one.

Soap is formed by the combination of a fatty acid with an alkali; it is manufactured by boiling oil or fat with potash or soda, the former for soft, the latter for hard soaps. In the preparation of ordinary hard soap, the soda takes from the oil or fat two acids, *stearic* and *oleic* acids, which exist in abundance in most varieties of fat, and unites with them to form soap, which in chemical language would be spoken of as a mixture of *stearate* and *oleate of soda*.

If soap be rubbed in soft water until a little of it has dissolved, and some Epsom salts (sulphate of magnesia) be dissolved in water, and poured into the soap water, curdy flakes will be produced, as when soap is rubbed in hard water, and the soap water will lose its property of frothing when stirred; the sulphate of magnesia has decomposed the soap, the soda contained in the latter has combined with the sulphuric acid existing in the sulphate of magnesia, to form a sulphate of soda which remains dissolved in the water, while the magnesia, uniting with the stearic and oleic acids, produces the insoluble curdy flakes which consist of stearate and oleate of magnesia.

Similar to the effect of the sulphate of magnesia is that of hard waters; their hardness is attributable to the presence of the different salts of lime and magnesia, all of which decompose the soap in the manner exemplified above; the peculiar properties of the soap in forming a lather and dissolving grease can, therefore, be manifested only when a sufficient quantity has been employed to decompose the whole of the salts of lime and magnesia contained in the quantity of water operated on, and thus a considerable amount of soap must be rendered useless when hard water is employed.

On examining the interior of a kettle in which spring, well, or river water has been boiled, it will be found to be coated more or less thickly with a *fur* or incrustation, generally of a brown colour, and the harder the water, the more speedily will this incrustation be deposited. A chemical examination shows this deposit to consist chiefly of carbonate of lime, in the form of minute crystals, which may be discovered by the microscope; it usually contains, in addition, some carbonate of magnesia, sulphate of lime, and small quantities of sesquioxide of iron (rust), and vegetable matter, the last two substances imparting its brown colour. In order to explain the formation of this deposit, it is necessary to become acquainted with the particular condition in which the carbonate of *lime exists in natural* waters. Carbonate of lime is hardly dissolved to

any perceptible extent by pure water, though it may be dissolved in considerable quantity by carbonic acid. This statement, which is of great importance in connexion with natural waters, may be verified in the following manner. A little slaked lime is well shaken up in a bottle of distilled or rain water, which is afterwards set aside for an hour or two; as soon as that portion of the lime which has not been dissolved has subsided, the clear portion is carefully poured into a glass, and a little soda-water or solution of carbonic acid in water is added to it; the first addition of the carbonic acid to the lime water causes a milkiness, due to the formation of minute particles of carbonate of lime, by the union of the carbonic acid with the lime; this carbonate of lime, being insoluble in the water, separates from it, or *precipitates*, and impairs the transparency of the liquid; a further addition of carbonic acid water renders the liquid again transparent, for the carbonic acid dissolves the carbonate of lime which has separated, forming, in the opinion of some chemists, a definite chemical compound, the *bicarbonate of lime*, which contains twice as much carbonic acid as the carbonate; since, however, this bicarbonate of lime has not been separated from the water in a pure state, it is safer to regard it merely as a solution of carbonate of lime in free carbonic acid.

If this clear solution be introduced into a flask, and boiled over the spirit-lamp or gas-flame, it will again become turbid, for the free carbonic acid will be expelled by the heat, and the carbonate of lime will be deposited, not now, however, in so fine a powder as before, but in small hard grains which have a tendency to fix themselves firmly upon the sides of the flask, and, when examined by the microscope, are seen to consist of small crystals.

In a similar manner, when natural waters are boiled, the free carbonic acid which they contain is expelled in the gaseous state, and the carbonates of lime, magnesia, and oxide of iron are precipitated, since they are insoluble in water which does not contain carbonic acid. But, by the ebullition of the water, a portion of it has been dissipated in vapour, and if there be much sulphate of lime present, the quantity of water left may not be sufficient to retain the whole of that salt in solution; and this is the more likely to happen, because sulphate of lime requires about 400 parts of water to dissolve it;* a quantity of sulphate of lime, then, is liable to be deposited together with the carbonates of lime, magnesia, and oxide of iron, and, should the water contain much vegetable matter, this is also often deposited in an insoluble condition, the whole eventually forming together a hard compact mass, composed of successive thin layers, on the bottom and sides of the vessel in which the water has been boiled. The "furring" of a kettle is objectionable, chiefly in consequence of its retarding the ebullition of the water, since the deposit is a very bad conductor of heat, and therefore impedes the transmission of heat from the fire to the water; hence the common practice of introducing a round stone or marble into the kettle, in order, by its perpetual rolling, to prevent the particles of carbonate of lime from forming a compact layer. In steam boilers, however, even more serious inconvenience than loss of time sometimes arises if this deposit be allowed to accumulate, and to form a thick layer of badly conducting material on the bottom of the boiler, since

* Sulphate of lime has been found nearly insoluble in water having a higher temperature than 212° F., as would be the case in boilers worked under pressure, so that it would readily be deposited. It is said that waters containing little or no sulphate of lime yield a loose and friable deposit.

the latter is then liable to become red hot, and should the incrustation happen to crack, and allow the water to reach the red hot metal, so violent a disengagement of steam follows, that boilers have been known to burst under the sudden pressure. But even though this calamity be escaped, the wear and tear of the boiler is very much increased in consequence of the formation of this deposit, since its hardness often renders it necessary to detach it with the hammer, much to the injury of the iron boiler-plates, which are also subject to increased oxidation and corrosion, in consequence of the high temperature which the incrustation permits them to attain by preventing their contact with the water. The exigency of the case has elicited many propositions for the prevention of these incrustations; some substances have been used of which the action appears to be purely mechanical, in preventing the aggregation of the deposited particles. Clay, saw-dust, and other matters have been employed with this view; but the action of sal-ammoniac, which has also been found efficacious, must be explained upon purely chemical principles. When this salt is boiled with carbonate of lime, mutual decomposition ensues, resulting in the production of chloride of calcium and carbonate of ammonia, of which salts the former is very soluble in water, while the latter passes off in vapour with the steam.*

The incrustations formed in cisterns and pipes by hard water are also produced by the carbonates of lime and magnesia deposited in consequence of the escape of the free carbonic acid which held them in solution. Many interesting natural phenomena may be explained upon the same principle. The so-called *petrifying springs*, in many cases, owe their remarkable properties to the considerable quantity of carbonate of lime dissolved in carbonic acid which they contain; when any object, a basket, for example, is repeatedly exposed to the action of these waters, it becomes coated with a compact layer of carbonate of lime, and thus appears to have suffered conversion into limestone. The celebrated waters of the Sprudel at Carlsbad, of San-Filippo in Tuscany, and of Saint Allyre in Auvergne, are the best instances of this kind.

Fig. 43.—Stalactite Cavern.

The *stalactites* and *stalagmites*,† which are formed in certain caverns or natural grottoes (fig. 43), afford beautiful examples of the gradual separation of the carbonate of lime from water charged with carbonic acid. Each drop of water, as it trickles through the roof of the

* $CaO.CO_2$ + $NH_3.HCl$ = $NH_3.HO.CO_2$ + $CaCl$
Carbonate of lime. Sal-ammoniac. Carbonate of ammonia. Chloride of calcium.
Solutions of the caustic alkalies, of alkaline carbonates, and arsenites, are also occasionally employed to prevent the formation of incrustations in boilers.

† *From σταλαζω, to drop; σταλαγμα, a drop.*

cavern, becomes surrounded with a shell of carbonate of lime, the length of which is prolonged by each drop as it falls, till a stalactite is formed, varying in colour according to the nature of the substances which are separated from the water together with the carbonate of lime (such as the oxides of iron and vegetable matter); and as each drop falls from the point of the stalactite upon the floor of the cavern, it deposits there another shell of carbonate of lime, which grows, like the upper one, but in the opposite direction, and forms a stalagmite, thus adorning the grotto with conical pillars of carbonate of lime, sometimes, as in the case of the *oriental alabaster*, variegated with red and yellow, and applicable to ornamental purposes.

When water which has been boiled for some time is compared with unboiled water from the same source, it will be found to have become much softer, and this can now be easily explained, for, a considerable proportion of the salts of lime and magnesia having separated from the water, the latter is not capable of decomposing so large a quantity of soap. The amount of hardness which is thus destroyed by boiling is generally spoken of as *temporary* hardness, to distinguish it from the *permanent* hardness due to the soluble salts of lime and magnesia which still remain in the boiled water. It is customary with analytical chemists, in reporting upon the quality of natural waters, to express the hardness by a certain number of degrees which indicate the number of grains of chalk or carbonate of lime which would be dissolved in a gallon of water containing carbonic acid, in order to render its hardness equal to that of the water examined, that is, to render it capable of decomposing an equal quantity of soap. Thus, when a water is spoken of as having 16 degrees hardness, it is implied that 16 grs. of carbonate of lime dissolved in a gallon of water, containing carbonic acid, would render that gallon of water capable of decomposing as much soap as a gallon of the water under consideration.

The utility of a water for household purposes must be estimated, therefore, not merely according to the total number of degrees of hardness which it exhibits, but also by the proportion of that hardness which may be regarded as temporary, that is, which disappears when the water is boiled. Thus the total hardness of the New River water amounts to nearly 15 degrees, that of the Grand Junction Company to 14 degrees, and yet these waters are quite applicable to household uses, since their hardness is reduced by boiling to about 5 degrees. It has been ascertained that every degree of hardness in water gives rise to a waste of about 10 grs. of soap for every gallon of water employed, and hence the use of 100 gallons of Thames or New River water in washing will be attended with the loss of about 2 lbs. of soap; this loss is reduced, however, to about one third when the temporary hardness has been destroyed by boiling. The addition of washing soda (carbonate of soda) removes not only the temporary, but also the permanent hardness due to the presence of the sulphates of lime and magnesia in the water, for both these salts are decomposed by the carbonate of soda, which separates the lime and magnesia as insoluble carbonates, while sulphate of soda remains dissolved in the water.* The household practice of boiling the water, and adding a little washing soda, is therefore very efficacious in removing the hardness. *Clark's process* for softening waters depends upon the neutralisa-

* $CaO.SO_3$ + $NaO.CO_2$ = $NaO.SO_3$ + $CaO.CO_2$
Sulphate of lime. *Carbonate of soda.* Sulphate of soda. Carbonate of lime.

tion of the free carbonic acid contained in the water by the addition of a certain quantity of lime; the lime thus added combines with the free carbonic acid, and the carbonate of lime so produced separates together with the carbonates of lime and magnesia, which were previously retained in solution by the free carbonic acid; this process, therefore, affects chiefly the temporary hardness; moreover, the earthy carbonates which are separated appear to remove from the water a portion of the vegetable matter which it contains, and thus effect a very important purification. The water under treatment is mixed in large tanks, with a due proportion of lime previously diffused through water (the quantity necessary having been determined by preliminary experiment), and the mixture allowed to settle until perfectly clear, when it is drawn off into reservoirs.*

Waters which are turbid from the presence of clay in a state of suspension, are sometimes purified by the addition of a small quantity of alum or sulphate of alumina, when the alumina is precipitated by the carbonate of lime, and carries down with it mechanically the suspended clay, leaving the water clear.

The *organic matter* contained in waters may be vegetable matter dissolved from the earth, with which it has come in contact, or resulting from the decomposition of plants, or it may be animal matter derived either from the animalcules and fish naturally existing in it, or from the sewage of towns, and, in the case of well waters, from surface drainage. It is a pretty generally received opinion that such of these organic matters as are very susceptible of chemical change have an injurious effect upon the system of persons drinking the water, and it is now usual, in examining water as to its fitness for consumption, to ascertain how much of the organic matter is in a changeable condition, by determining with the aid of a solution of permanganate of potash the amount of oxygen necessary to effect its conversion into more stable forms.

41. One of the most important points to be taken into account in estimating the qualities of a water is its action upon lead, since this metal is unfortunately so generally employed for the storage and transmission of water, and cases frequently occur in which the health has been seriously injured by repeated small doses of compounds of lead taken in water, which has been kept in a leaden cistern. If a piece of bright, freshly scraped lead be exposed to the air, it speedily becomes tarnished from the formation of a thin film of the oxide of lead, produced by the action of the atmospheric oxygen; this oxide of lead is soluble in water to some extent, and hence, when lead is kept in contact with water, the oxygen which is dissolved in it acts upon the metal, and the oxide so produced is dissolved by the water; but, fortunately, different waters act with very different degrees of rapidity upon the metal, according to the nature of the substances which they contain.

The film of oxide which forms upon the surface of the lead is insoluble, or nearly so, in water containing much sulphate or carbonate of lime, so that hard waters may generally be kept without danger in leaden cisterns; but soft waters, and those which contain nitrites or nitrates, should not be drunk after contact with lead. Nearly all waters which have been stored in leaden cisterns contain a trace of the metal, and since the action of this poison, in minute doses, upon the system is so gradual

* Thames and New River water are softened, in this way, to 3°·5, or to a lower point *than by an hour's boiling.*

that the mischief is often referred to other causes, it is much to be desired that lead should be discarded altogether for the construction of cisterns.

Mineral waters, as they are popularly called, are simply spring waters containing so large a quantity of some ingredient as to have a decided medicinal action. They are differently named according to the nature of their predominating constituent. Thus, a *chalybeate* water contains a considerable quantity of a salt of the oxide of iron (usually the carbonate dissolved by free carbonic acid); an acidulous water is distinguished by a large proportion of carbonic acid, and is well exemplified in the celebrated Seltzer water; a sulphureous or hepatic water has the nauseous odour due to the presence of sulphuretted hydrogen. The Harrowgate water is eminently sulphureous. Saline waters are such as contain a large quantity of some salt; thus the saline springs of Cheltenham are rich in common salt and sulphate of soda.

The chalybeate waters, which are by no means uncommon, become brown when exposed to the air, and deposit a rusty sediment which consists of the sesquioxide of iron, formed by the union of the oxygen of the air with the oxide of iron existing in the carbonate.*

42. *Sea water* contains the same salts as are found in waters from other natural sources, but is distinguished by the very large proportion of chloride of sodium (common salt). A gallon of sea water contains usually about 2500 grains of saline matter, of which 1890 grains consist of common salt. The circumstance that clothes wetted with sea water never become perfectly dry is to be ascribed chiefly to the *chloride of magnesium* present in the water, which is distinguished by its tendency to *deliquesce* or become damp in moist air. There are two elements, *bromine* and *iodine*, which are found combined with metals in appreciable quantity in sea water, though they are of somewhat rare occurrence in other waters derived from natural sources.

43. By *distillation*, pure water may be obtained from most spring and river waters.

(DEF.—*Distillation* is the conversion of a liquid into a vapour, and its recondensation into the liquid form in another vessel.)

Fig. 44.

Fig. 44 represents the ordinary form of still in common use, in which A is a copper boiler containing the water to be distilled; B the *head* of the still, which lifts out at *b*, and is connected by the

* $2(FeO, CO_2) + O + HO = Fe_2O_3.HO + 2CO_2$

Carbonate of iron. Water. Hydrated sesquioxide of iron. Carbonic acid.

neck C with the *worm* D, a pewter pipe coiled round in the tub E, and issuing at F. The steam from the boiler, passing into the worm, is condensed to the liquid state, being cooled by the water in contact with the worm; this water, becoming heated, passes off through the pipe G, being replaced by cold water, which is allowed to enter through H.*

Another form of apparatus for distillation of water and other liquids is shown in fig. 45. A is a stoppered *retort*, the neck of which fits into the tube of a *Liebig's condenser* (B), which consists of a glass tube (C) fitted by means of corks into a glass, copper, or tin tube (D), into which a stream of cold water is passed by the funnel E, the heated water running out through the upper tube F. The water furnished by the condensation of the steam passes through the *quilled receiver* G, into the flask H. Heat is gradually applied to the retort by a ring gas-burner.

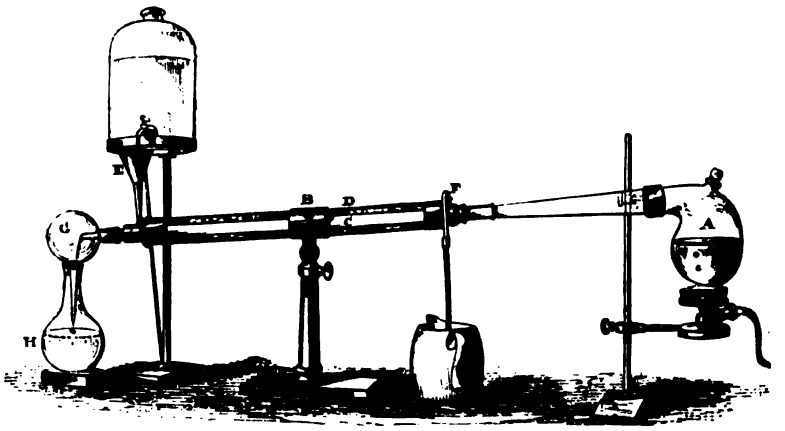


Fig. 45.—Distillation—Liebig's condenser.

Many special precautions are requisite in order to obtain absolutely pure distilled water for refined experiments, but for ordinary purposes the common methods of distillation yield it in a sufficiently pure condition.

The saline matters present in the water are of course left behind in the still or retort. Sea water is now frequently distilled on board-ship when fresh water is scarce. The vapid and disagreeable taste of distilled water, which is due to its having been deprived of the dissolved air during the distillation, is remedied by the use of Normandy's apparatus, which provides for the restoration of the expelled air.

44. The physical properties of water are too well known to require any detailed description. Its specific gravity in the liquid state is = 1, being taken as the standard to which the specific gravities of liquid and solid bodies are referred.

(DEF.—The *specific gravity of a liquid or solid body* is its weight as compared with that of an equal volume of pure water at 60° F., 15°·5 C.)

Water assumes the solid form, under ordinary circumstances, at 32° F. (0° C.), and may be obtained in six-sided prismatic crystals. Snow consists of beautiful stellate groupings of these crystals. Ice has the specific gravity 0·9184. In the act of freezing, water expands very considerably, so that 174 volumes of water become 184 volumes of ice. The breakage of vessels, splitting of rocks, &c., by the congelation of water, are due to

* A rosette gas-burner (K) on Bunsen's principle is very convenient for a small still of this description.

this expansion. Water passes off in vapour at all temperatures, the amount of vapour evolved in a given time of course increasing with the temperature. The boiling-point of water is 212° F. (100° C.)

(DEF.—The *boiling-point* of a liquid is the constant temperature indicated by a thermometer, the bulb of which is immersed in the boiling liquid in the presence of a coil of platinum wire, to facilitate disengagement of vapour, and at a pressure of 30 in. (762 Mm.) Bar.)

At and above 212° F. at the ordinary atmospheric pressure (30 in. Bar.), water is an invisible vapour of specific gravity 0·622 (air = 1). One cubic inch of water at 60° F. becomes 1696 cubic inches of vapour at 212° F.

45. In its chemical relations water presents this very remarkable feature, that, although it is an *indifferent oxide*, its combining tendencies extend over a wider range than those of any other compound. Its combinations with other substances are generally called *hydrates*. Water combines with two of the elementary substances, viz., chlorine and bromine, forming an exception to the general rule that *combination does not take place between elementary and compound bodies*. No other element is even *dissolved* by water in any considerable quantity. One part of iodine is dissolved by 7000 parts of cold water, but no chemical combination appears to take place. Oxygen, hydrogen, and nitrogen are dissolved by water in very small quantity, but become only mechanically diffused through it, and do not enter into chemical combination.

When water acts upon a compound body, it may either effect a *simple solution*, or may enter into chemical combination with it.

Simple solution appears to be a purely physical phenomenon, not accompanied, of necessity, by any chemical action. The dissolved substance, in such cases, is otherwise unchanged in properties, and there is no manifestation of heat, as in cases of chemical combination. On the contrary, there is a reduction of temperature, such as is always noticed in the merely physical change from the solid to the liquid form. For example, common saltpetre (nitre or nitrate of potash, $KO.NO_5$), when shaken with water, is rapidly dissolved, the water becoming sensibly colder. If fresh portions of saltpetre be added till the water is unable to dissolve any more, it will be found that 1000 grs. of water (at 60° F.) have dissolved about 300 grs. of saltpetre. Such a solution would be called a *cold saturated solution* of saltpetre. If the solution be set aside in an open vessel, the water will slowly pass off in vapour, and the saltpetre will be gradually deposited, its particles arranging themselves in the regular geometrical shape of the six-sided prism, which is its common *crystalline form*. The crystals of saltpetre do not contain any water; they are *anhydrous*.

Fig. 46.

If saltpetre be added to boiling water (in a porcelain evaporating dish, fig. 46), and stirred (with a glass rod) until the water refuses to dissolve any more, 1000 grs. of water will be found to have dissolved about 2000 grs.; this would be called a *hot saturated solution*.

As a general rule, solids are dissolved more quickly and in larger quantity by hot water *than by cold*.

One of the commonest methods of *crystallising* a solid substance consists in dissolving it in hot water, and allowing the solution to cool slowly. The more slowly it cools, the larger and more symmetrical are the crystals. A hot saturated solution is not generally the best for crystallising, because it deposits the dissolved body too rapidly. Thus, the hot solution of saltpetre prepared as above would solidify to a mass of minute crystals on cooling; but if 1000 grs. of saltpetre be dissolved in 4 measured ounces of boiling water, it will form crystals of 2 or 3 inches long when slowly cooled (in a covered vessel). If the solution be stirred while cooling, the crystals will be very minute, having the appearance of a white powder.

Some solids, however, refuse to crystallise, even from a hot saturated solution, if it be kept absolutely undisturbed.

Sulphate of soda affords a good example of this. If the crystallised sulphate be added to boiling water in a flask, as long as it is dissolved, the water will take into solution more than twice its weight of the salt. If this solution be allowed to cool in the open flask, an abundant crystallisation will take place, for cold water will dissolve only about one-third of its weight of crystallised sulphate. But if the flask (which should be globular) be tightly corked whilst the solution is boiling, it may be kept for several days without crystallising, although moved about from one place to another. In this condition the solution is said to be *super-saturated*. On withdrawing the cork, the air entering the partly vacuous space above the liquid will be seen to disturb the surface slightly, and from that point beautiful prismatic crystals will shoot through the liquid until the whole has become a nearly solid mass. A considerable elevation of temperature is observed, consequent upon the passage from the liquid to the solid form. If the solution of sulphate of soda be somewhat weaker, containing exactly two-thirds of its weight of the crystals, it may be cooled without crystallising, even in vessels covered with glass plates, but a touch with a glass rod will start the crystallisation immediately.*

In the laboratory, stirring is always resorted to in order to induce crystallisation, if it does not take place spontaneously. Thus it is usual to test for potash in a solution by adding tartaric acid, which should cause the formation of minute crystals of *bitartrate of potash* (*cream of tartar*), but the test seldom succeeds unless the solutions are briskly stirred together with a glass rod. An amusing illustration of this is afforded by pouring a solution of tartaric acid into a solution of saltpetre, and allowing the clear mixture to run over a large plate of glass. Letters traced on the glass with the finger will now be rendered visible by the deposition of the crystals of bitartrate of potash upon the glass.

46. The crystals of sulphate of soda produced in the above experiments contain, in a state of combination with the salt, more than half their weight of water. Their composition is

Anhydrous sulphate of soda ($NaO . SO_3$)	71 parts,	or one combining weight,
Water	90 „	or ten combining weights,

as expressed by the formula $NaO . SO_3 + 10\ HO$. If some of the crystals be pressed between blotting paper to remove adhering water, and left exposed to the air, they will gradually *effloresce*, or become covered with a white opaque powder. This powder is the anhydrous sulphate of soda into which the entire crystals would ultimately become converted by exposure to air. Since most crystals containing water have their crystalline form destroyed or modified by the loss of the water, it is commonly spoken of as *water of crystallisation*.

Coloured salts, containing water of crystallisation, generally change colour when the water is removed. The *sulphate of copper* (*blue stone*)

* It is very remarkable that, if the glass rod has been recently heated, it will not cause *the crystallisation* even after it has been cool for some time.

fords an excellent example of this. The beautiful blue prismatic crystals f this salt contain

Anhydrous sulphate of copper ($CuO . SO_3$)	79·8 parts,	or one combining weight,
Water	45·0 „	or five combining weights,

s expressed by the formula $CuO . SO_3 + 5HO$.

When these are exposed to the air at the ordinary temperature they main unchanged; but if heated to the boiling-point of water, they ecome opaque, and may be easily crumbled down to a white powder. his powder contains

Anhydrous sulphate of copper ($CuO . SO_3$)	79·8 parts,	or one combining weight,
Water	9 „	or one combining weight,

nd would therefore be represented by $CuO . SO_3 + HO$. The four comining weights of water, which have been expelled, constituted the water f crystallisation, upon which the form and colour of the sulphate of opper depend. If the white powder be moistened with water, comination takes place, with great evolution of heat, and the blue colour is reproduced. The one combining weight of water which still remains, is ot expelled until the salt is heated to 390° F. (199° C.), proving that it held to the sulphate of copper by a more powerful chemical attraction. n this account it is spoken of as *water of constitution*, and in order that he formula of the salt may exhibit the difference between the water of onstitution and of crystallisation, it is usually written—

$$CuO . SO_3 . HO + 4Aq.*$$

(Def.—*Water of crystallisation* of salts is that which is generally xpelled at 212° F. (100° C.), and is connected with the form and colour f the crystals. *Water of constitution* is not generally expelled at 212° F., nd is in more intimate connexion with the chemical properties of the salt.)

Several of the so-called *sympathetic inks* employed for writings which re invisible until heated, depend upon the change of colour which results rom the loss of water of crystallisation. Characters written with a weak olution of chloride of cobalt and allowed to dry are very nearly invisible, since the pink colour of so small a quantity of the salt is scarcely oticed; but on warming the paper, the pink hydrated chloride of cobalt ($CoCl + 2Aq.$) loses its water of crystallisation, and the blue anhydrous hloride of cobalt is produced. On exposure to air this again absorbs ater, and the writing fades away.

Some salts have so great a tendency to combine with water, that they ecome moist or *deliquesce* when exposed to air. This *deliquescence* is xhibited in a marked degree by *chloride of calcium*, and its great attracion for water is turned to advantage in drying air and other gases by assing them through tubes filled with the salt.

47. Most bases are capable of combining with water to form hydrates, s exemplified in the slaking of lime. Anhydrous lime or quick-lime (CaO), when wetted with water, combines with it, evolving much heat, nd crumbling to a loose bulky powder, which is hydrate of lime or slaked ime ($CaO . HO$). At a red heat the water is expelled, and anhydrous ime remains.

* *Aqua*, water.

The hydrates of potash, soda, and baryta, however, do not lose their water when heated, which has led some chemists to entertain the belief that they do not really contain water as such, but that they have been formed from water by the substitution of a metal for a portion of its hydrogen. Upon this view, the hydrate of potash, instead of being represented by the formula KO . HO, would be KHO_2,* or two combining weights of water (H_2O_2), in which potassium has been substituted for half the hydrogen. In representing chemical changes by equations, much convenience often results from the adoption of this formula; but as the same view would have to be taken of those hydrates which hold their water very loosely, we may question the propriety of insisting upon the above view of the constitution of hydrate of potash, &c., as a fact rather than a convenient hypothesis.

48. Nearly all the acids are capable of forming hydrates. Indeed, as a general rule, the hydrated form of an acid is that in which it is commonly obtained and used, the anhydrous acid being usually of very secondary importance. Thus, the liquid used under the name of concentrated sulphuric acid is the hydrate of that acid (HO . SO_3), the anhydrous sulphuric acid (SO_3) being a crystalline solid of no use except to the chemist, and not manifesting any acid properties until brought into contact with water, with which it combines with evolution of much heat. The hydrated sulphuric acid (HO . SO_3) does not lose its water when heated, but distils unchanged, and some chemists are of opinion that the hydrogen is not contained in it in the form of water, but that the so-called hydrated sulphuric acid should be represented as HSO_4,† so as not to indicate that it contains water. The acid is thus represented as a *unitary* compound (formed of one group), instead of a *binary* compound of the groups HO and SO_3. Convenient as this view is sometimes found in notation and in theoretical speculations, the circumstance that SO_3 is known in the separate state, and yields the hydrated sulphuric acid when brought in contact with water, causes the latter view still to find favour among practical chemists.

The hydrated sulphuric acid (HO . SO_3) has a very powerful attraction for more water, which leads to its employment in the laboratory for drying air and gases, as well as for producing many chemical changes which depend upon the abstraction of water or its elements (*dehydration*). If concentrated sulphuric acid (*oil of vitriol*) be poured into water, the mixture will become very hot, in consequence of the combination between the two liquids. The water should be stirred whilst the acid is being poured in, as the sudden mixture of considerable quantities might cause danger from the projection of the liquid.

49. *Binoxide* or *peroxide of hydrogen* or *oxygenated water*, HO_2.‡ This compound is not met with in nature, nor has it any important useful application in the arts. It has recently, however, acquired some importance as a medicinal agent, and it possesses very great interest for the student of chemical philosophy, because it helps to throw some light upon the atomic constitution of the elements.

The easiest and most interesting method of obtaining oxygenated water (though not in the pure state), consists in exposing a few freshly scraped sticks of phosphorus to the air, at the bottom of a large jar,§ with enough water to cover one-half

* Or, if $\Theta = 16$, by $KH\Theta$.

† Or, if $\Theta = 16$ and $S = 32$, as $H_2S\Theta_4$.

‡ Or, if $\Theta = 16$, the formula of peroxide of hydrogen will be $H_2\Theta_2$.

§ The phosphorus may be placed upon a porcelain colander, which is supported on the surface of two or three ounces of water in a dish, and freely exposed to the open air.

cks. The jar should be loosely covered, and the air renewed by blowing casionally. It should also be placed in a situation where no injury would the phosphorus were to take fire and crack the jar. Of course ozone will be l in abundance in the air of the jar, and in the course of a few days the ll be highly charged with phosphorous and phosphoric acids, and will have a considerable amount of oxygen from the air. If a test-tube or small be filled with this water, a little powdered binoxide of manganese thrown nd the tube then quickly closed and inverted with its mouth under water, ervescence will ensue from the escape of oxygen which will collect in the l may be recognised by the usual test with a partly extinguished match. oxide of manganese does not appear to be decomposed in this experiment, e of the oxygen being derived from the binoxide of hydrogen dissolved ater, which is immediately decomposed, by contact with the binoxide of se, into water and free oxygen. If a solution of permanganate of potash (Mn_2O_7), which owes its red colour to the permanganic acid (Mn_2O_7), be poured inder partly filled with the liquid, it will cause a rapid evolution of oxygen, not only from the binoxide of hydrogen, but from the permanganic acid, olour of which disappears, because it becomes reduced to a lower oxide of se.

ual method of preparing binoxide of hydrogen in a pure state, consists in ing the binoxide of barium with diluted hydrochloric acid, under certain ns to avoid the decomposition of the very unstable binoxide of hydrogen. tion is represented by the equation $BaO_2 + HCl = HO_2 + BaCl$. The of barium is removed from the solution by the cautious addition of sulphate which precipitates the barium as sulphate of baryta, and the silver as of silver, thus, $BaCl + AgO . SO_3 = AgCl + BaO . SO_3$. The precipitates ed to subside, and the clear liquid evaporated in the exhausted receiver of ump over a dish of oil of vitriol to absorb the water, which evaporates much idly than the binoxide. The pure binoxide of hydrogen is a syrupy liquid 1·453, with a very slight chlorous odour. Its most remarkable feature is ty with which it is decomposed into water and oxygen.* Even at 70° F. to evolve bubbles of oxygen, so that it can scarcely be prepared in hot At 212° it decomposes with violence. The mere contact with certain uch as gold, platinum, and silver, which have no direct attraction for oxy- cause the decomposition of the binoxide of hydrogen, without any chemical of the metal itself.† It was noticed above that the binoxide of manganese es it without undergoing any apparent change. The most surprising hat which takes place with oxide of silver. If a drop of binoxide of hydro- llowed to fall upon oxide of silver, which is a brown powder, decomposition ce with explosive violence and great evolution of heat, the oxide of silver s oxygen, and becoming grey metallic silver. The oxides of gold and are acted upon in a similar manner.

very extraordinary changes, which were formerly described as *catalytic* re now generally accounted for by the hypothesis that the oxygen in the silver, &c., exists in a condition different from that of the second equivalent in the binoxide of hydrogen, and that these two conditions of oxygen hemical attraction for each other, similar to that which exists between elements. If the oxygen in the oxide of silver be represented as *electro-* xygen (see 22), as its relation to the metal would lead us to expect, and d atom of oxygen in the binoxide of hydrogen be represented as *electro-* xygen, the mutual decomposition of the two compounds might be repre- the equation,

$$\underset{-}{AgO} + H\underset{+}{OO} = Ag + HO + \underset{-+}{OO}.$$

ules—Molecular formulæ.—This would lead to the belief that in its ordinary condition, as it exists in the atmosphere, is really *of oxygen*, consisting of two atoms of oxygen in opposite states,

presence of a little free acid renders it rather more stable, whilst free alkali has ite effect. A solution of peroxide of hydrogen, containing a little hydrochloric w sold for medicinal and photographic uses.

inexplicable changes as this are sometimes included under the general denomina- *talysis, or decomposition by contact.*

and that the smallest particle of oxygen which can exist in the separate state is really composed of two atoms. This *smallest particle of free oxygen* would be appropriately termed a *molecule* of oxygen, whilst an *atom* of oxygen would be defined as the *smallest particle which can exist in a state of combination.* If the *atomic weight* of oxygen were taken to be 16, the *molecular weight* would be 32. It will be seen hereafter that there are reasons for extending this view to the constitution of some other elements, and an opinion has been propounded, somewhat in advance of existing experimental evidence, that direct combination of elements is really a double decomposition where the corresponding atoms are exchanged. According to this view, the formation of water by the combination of hydrogen with oxygen would be expressed by the equation,

$$\overset{+}{H}\overset{-}{H} + \overset{+}{O}\overset{-}{O} = \overset{+}{H}\overset{-}{O} + \overset{-}{H}\overset{+}{O}$$

$$\text{or } H_2 + O_2 = H_2O_2$$

and the *molecule* of water, or the smallest particle capable of existing in a free state, or of resulting from chemical action, would be represented by H_2O_2, and would weigh 18 parts (H = 1), or if O = 16 parts of oxygen, by H_2O.

It has been suggested that ozone is really the negative atom of oxygen detached from the positive atom or *antozone* associated with it in the molecule $\left(\overset{-}{O}\,\overset{+}{O}\right)$, and this view is supported by the circumstance, that binoxide of hydrogen appears to be formed in all cases where ozone is produced by slow oxidation in the presence of water, making it appear probable that the latter (HO) combines with the *antozone* to form binoxide of hydrogen $\left(\overset{+}{HO}\overset{+}{O}\right)$ whilst the ozone $\overset{-}{O}$ is eliminated in the free state. The production of ozone in the electrolysis of water (see 23), appears also to be attended by that of binoxide of hydrogen. Upon this view of the nature of ozone, however, it would not be easy to explain the contraction which pure dry oxygen has been found to suffer during partial conversion into ozone by the action of the electric discharge, or the circumstance, that when a mixture of oxygen and ozone so produced is exposed to the action of mercury, no diminution of volume is observed, although the metal removes the ozone, combining with it to form an oxide of mercury. Both these, however, would be explicable on the theory that ozone is really formed by a coalition of atoms of oxygen, to produce a compound which may be represented as binoxide of hydrogen (HOO), in which the hydrogen is replaced by oxygen, forming (OOO); then, just as two volumes of hydrogen combining with one volume of oxygen contract to two volumes of steam, it might be supposed that two volumes of oxygen combining with one volume of oxygen, would contract to two volumes of ozone, and just as on decomposing two volumes of steam with a metal, two volumes of hydrogen are left, so on decomposing the two volumes of ozone with a metal two volumes of oxygen would be liberated, and no contraction observed.* Reasoning analogically from the properties of binoxide of hydrogen, this theory would also enable us to explain the easy reconversion of ozone by heat, and by the action of binoxide of manganese.† The occurrence of binoxide of hydrogen in so many cases of the production of ozone would also favour this view.

* Some recent experiments have indicated that the specific gravity of ozone is just what this theory would require, that is, half as great again as that of ordinary oxygen, or 1·66.

† Finely divided platinum, which causes decomposition of binoxide of hydrogen, has also been found to destroy ozone.

CARBON.

his element is especially remarkable for its uniform presence in ubstances. The ordinary laboratory test by which the chemist whether a substance under examination is of organic origin, n heating it with limited access of air, and observing whether kening from separation of carbon (*carbonisation*) ensues.

ements are capable of assuming so many different aspects as carbon. with transparent and colourless in the *diamond*, opaque, black, and tallic in *graphite* or black lead, velvety and porous in wood-*charcoal*, r new conditions in *anthracite*, *coke*, and *gas-carbon*.

ture, free carbon may be said to occur in the forms of diamond, and anthracite (the other varieties of coal containing considerable ns of other elements).

from its great beauty and rarity, the diamond possesses a special n chemical eyes, from its having perplexed philosophers up to le of the last century, notwithstanding the simplicity of the ex- s required to demonstrate its true nature. The first inkling of it o have been obtained by Newton, when he perceived its great refracting light, and thence inferred that, like other bodies g that property in a high degree, it would prove to be com- ("an unctuous substance coagulated"). When this prediction fied, the burning of diamonds was exhibited as a marvellous nt, but no accurate observations appear to have been made till ien Lavoisier ascertained, by burning diamonds suspended in the burning-glass, in a confined portion of oxygen, that they were en- verted into carbonic acid gas. In more recent times this experi- been repeated with the utmost precaution, and the diamond has rly demonstrated to consist of carbon in a crystallised state.

nore important result of this experiment was the exact determination of sition of carbonic acid, without which it would not be possible to ascertain e proportion of carbon in any of its numerous compounds, since it is always n that form.

st accurate experiments upon the synthesis of carbonic acid have been with the arrangement represented in fig. 47.

the porcelain tube A, which is heated to redness in a charcoal fire, was ttle platinum tray, accurately weighed, and containing a weighed quantity ts of diamond. One end of the tube was connected with a gas-holder B, oxygen which was thoroughly purified by passing through the tube C, potash (to absorb any carbonic acid and chlorine which it might contain), by passing over pumice soaked with concentrated sulphuric acid in D and e other end of the porcelain tube, A, there was attached a glass tube F, d in a furnace, and containing oxide of copper, to convert into carbonic arbonic oxide which might have been formed in the combustion of the The carbonic acid was then passed over pumice soaked with sulphuric to remove any traces of moisture, and afterwards into a weighed bulb- H, containing solution of potash, and two weighed tubes I K, containing, ly, solid hydrate of potash and sulphuric acid on pumice, to guard against e of aqueous vapour taken up by the excess of oxygen in its passage ie bulbs H. The increase of weight in H, I, K, represented the carbonic d in the combustion of an amount of diamond indicated by the loss of ffered by the platinum tray, and the difference between the diamond and the carbonic acid formed would express the amount of oxygen which ned with the carbon. A large number of experiments conducted in this oth with diamond and graphite, showed that 6 parts of carbon furnished carbonic acid, and consumed, therefore, 16 parts of oxygen.

inary mode of exhibiting the combustion of the diamond on the lecture

table, consists in suspending it within a double loop of platinum wire attached to an iron wire passing through a deflagrating-collar, and heating it in a jet of oxygen

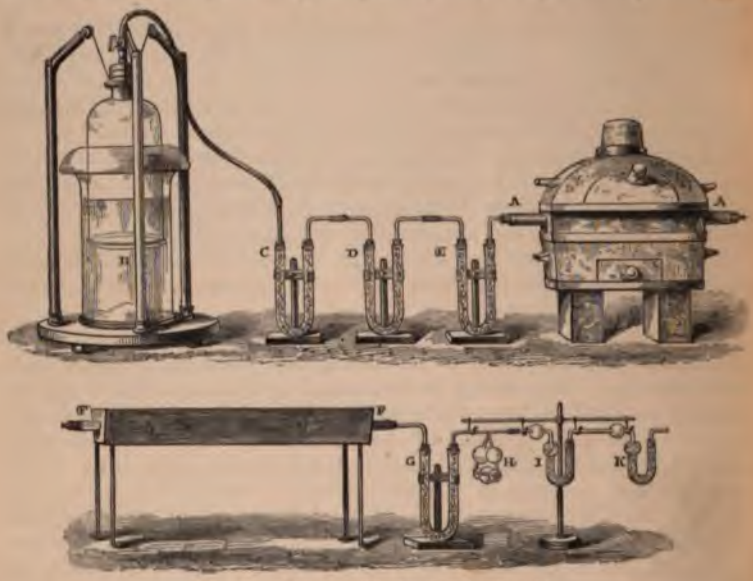


Fig. 47.—Exact synthesis of carbonic acid.

sent through a gas or spirit flame (fig. 48). As soon as it has attained a white heat, the diamond is plunged into a globe of oxygen, and after burning for a few seconds, it is withdrawn, and a little lime-water is shaken in the globe to produce the milky

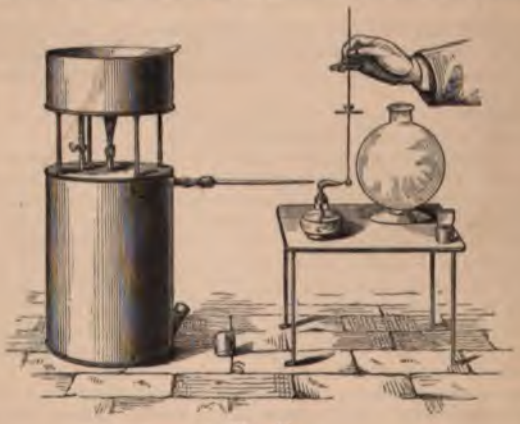


Fig. 48.

deposit of carbonate of lime. It not unfrequently happens that the blowpipe flame fuses the platinum wire, and the diamond drops out before it can be immersed in the oxygen. A more convenient arrangement is shown in fig. 49. The diamond is supported in a short helix of platinum wire A, which is attached to the copper wires B B, passing through the cork C, and connected with the terminal wires of a Grove's battery of five or six cells. The globe having been filled with oxygen by *passing the gas down* into it till a match indicates that the excess of oxygen is

streaming out of the globe, the cork is inserted, and the wires connected with the battery. When the heat developed in the platinum coil, by the passage of the current, has raised the diamond to a full red heat, the connexion with the battery may be interrupted, and the diamond will continue to burn with steady and intense brilliancy.

Fig. 49.

To an observer unacquainted with the satisfactory nature of this demonstration, it would appear incredible that the transparent diamond, so resplendent as to have been reputed to emit light, should be identical in its chemical composition with graphite (*plumbago* or *black lead*) from which, in external appearance, it differs so widely. For this difference is not confined to their colour; in crystalline form they are not in the least alike, the diamond occurring generally in octahedral crystals, while graphite is found either in *amorphous* masses (that is, having no definite crystalline form), or in six-sided plates which are not geometrically allied with the form assumed by the diamond. Carbon, therefore, is *dimorphous*, or occurs in two distinct crystalline forms. Even in weight, diamond and graphite are very dissimilar, the former having an average specific gravity of 3·5, and the latter of 2·3. Again, a crystal of diamond is the hardest of all substances, whence it is used for cutting and for writing upon glass, but a mass of graphite is soft and easily cut with a knife. The diamond is a non-conductor of electricity, but the conducting power of graphite renders it useful in the electrotype process.

Diamonds are chiefly obtained from Golconda, Borneo, and the Brazils. They usually occur enveloped in sandstone or quartz pebbles, which appear to have been rounded by attrition in the beds of running streams. The hardness of the diamond renders it necessary to employ diamond-dust for the purpose of cutting and polishing it, which is effected with the aid of a revolving disk of steel, to the surface of which the diamond-dust is applied in the form of a paste made with oil. The crystal in its natural state is best fitted for the purpose of the glazier, for its edges are usually somewhat curved, and the angle formed by these cuts the glass deeply, while the angle formed by straight edges, like those of an ordinary jeweller's diamond, is only adapted for scratching or writing upon glass. The diamond-dust used for polishing, &c., is obtained from a dark amorphous diamond found at Bahia in the Brazils; 1000 ounces annually are said to have been occasionally obtained from this source. When burnt, the diamond always leaves a minute proportion of ash of a yellowish colour in which silica and oxide of iron have been detected.

Although the diamond, when preserved from contact with the air, may be heated very strongly in a furnace, without suffering any change, it is not proof against the intense heat of the discharge taking place between two carbon points attached to the terminal wires of a powerful galvanic battery. If the experiment be performed in a vessel exhausted of air, the diamond becomes converted into a black coke-like mass which closely resembles graphite in its properties.

Graphite always leaves more ash than the diamond, consisting chiefly of the oxides of iron and manganese, with particles of quartz, and sometimes titanic acid. The purest specimens are those of compact amorphous graphite from Borrowdale in Cumberland; an inferior variety, imported from Ceylon, is crystalline, being composed of hexagonal plates. Graphite is obtained artificially in the manufacture of cast iron: in some

cases, a portion of the carbon of the cast iron separates in cooling in the form of crystalline scales of graphite, technically called *kish*. In the grey variety of cast iron these scales of graphite are diffused through the mass of the metal, and are left undissolved when the iron is dissolved by an acid.

Graphite is far more useful than the diamond, for, in addition to its application in black lead pencils, and for covering the surface of iron in order to protect it from rust, it is largely employed, in admixture with clay, for the fabrication of the black lead crucibles or *blue pots*, as they are commonly called, which are so valuable to the metallurgist, for their power of resisting high temperatures. Graphite is also sometimes employed for lubricating, to diminish friction in machinery, and for *facing* or imparting a fine glazed surface to gunpowder.

(Anthracite and the other varieties of coal will be described in a separate section.)

51. Several varieties of carbon, obtained by artificial processes, are employed in the arts. The most important of these are *lamp black*, *wood charcoal*, and *animal charcoal*.

Lamp black approaches more nearly in composition to pure carbon than either of the others, and is the soot obtained from the imperfect combustion of resinous and tarry matters (or of highly bituminous coal), from which source it derives the small quantities of resin, of nitrogen, and sulphur which it contains. The uses of this substance, as an ingredient of pigments, of printing ink, and of blacking, depend evidently more upon its black colour than upon its chemical properties.

Wood charcoal presents more features which arrest the attention of the chemist, as well on account of its specific properties, as of the influence exercised by the method adopted for obtaining it, upon its fitness for the particular purpose which it may be destined to serve.

If a piece of wood be heated in an ordinary fire, it is speedily consumed, with the exception of a grey ash consisting of the incombustible mineral substances which it contained; if the experiment were performed in such a manner that the products of combustion of the wood could be collected, these would be found to consist of carbonic acid and water, woody fibre is composed of carbon, hydrogen, and oxygen ($C_{12}H_{10}O_{10}$), and when it is burnt, the oxygen, in conjunction with more oxygen derived from the air, converts the carbon and hydrogen into carbonic acid and water. But if the wood be heated in a glass tube, closed at one end, it will be found impossible to reduce it, as before, to an ash, for a mass of charcoal will remain, having the same form as that of the piece of wood; in this case, the oxygen of the air not having been allowed free access to the wood, no true combustion has taken place, but the wood has undergone *destructive distillation*, that is, its elements have arranged themselves, under the influence of the high temperature, into different forms of combination, for the most part simpler in their chemical composition than the wood itself, and capable, unlike the wood, of enduring that temperature without decomposition; thus, it is merely an exchange of an unstable for a stable equilibrium of the particles of matter composing the wood.

(DEF.—*Destructive distillation* is the resolution of a complex substance into simpler forms under the influence of heat, out of contact with air.)

The vapours issuing from the mouth of the tube will be found acid

ius paper; they have a peculiar odour, and readily take fire with flame. These will be more particularly noticed here- ey contain some very useful substances. The charcoal which ot pure carbon, but contains considerable quantities of oxygen en, with a little nitrogen, and the mineral matter or ash of

e charcoal is to be used for fuel, it is generally prepared by which the heat developed by the combustion of a portion l is made to effect the charring of the rest. With this view f wood are built up into a heap (fig. 50) around stakes driven round, a passage so that the heap lled in the centre. l of wood, which from 30 to 40 feet is closely covered d sand, except for around the base, left uncovered to o the vapour of led from the wood in the first stage of the process. When is been kindled in the centre, the passage left for this pur- fully closed up. After the combustion has proceeded for and it is judged that the wood is perfectly dried, the open base is also closed, and the heap left to smoulder for three ks, when the wood is perfectly carbonised. Upon an average, charcoal are obtained by this process from 100 of wood.

Fig. 50.—Charcoal heap.

re economical process for preparing charcoal from wood consists it in an iron case or *slip* (F, fig. 51) placed in an iron re- which the gases and conducted by the pipe urnace B, where they d.

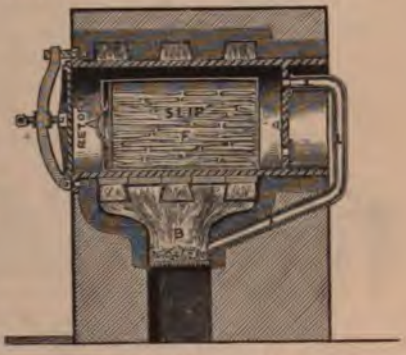


Fig. 51.—Charcoal retort.

mall scale, the opera- conducted in a glass own in fig. 52, where tar, and naphtha are the globular receiver, ammable gases are col- water.

ibility of the charcoal accounts for its very ty, upon which some emarkable and useful epend. The applica- coal for the purpose of "sweetening" fish and other fo- pient putrefaction has long been practised, and mo been employed for *deodorising* all kinds of put imal or vegetable matter. This property of char wer of absorbing into its pores very considerable specially of those which are easily absorbed by nch of charcoal is capa absorbing al *mmonia gas and 50 cub* of sulphu

both which are conspicuous among the offensive results of putr tion. This condensation of gases by charcoal is a mechanical effect, does not involve a chen combination of the cha with the gas; it is exhil most powerfully by coal which has been cently heated to redne a closed vessel, and c out of contact with ai plunging it under mer Eventually the offe gases absorbed by the coal are chemically acte

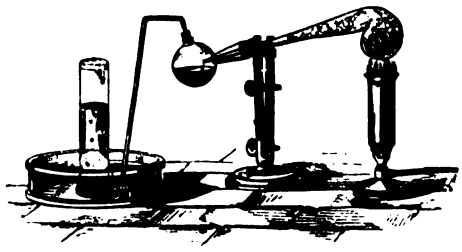


Fig. 52.—Distillation of wood.

by the oxygen of the air in its pores. A cubic inch of wood charcoal ab nearly 10 cubic inches of oxygen, and when the charcoal containing th thus condensed is presented to another gas which is capable of under oxidation, this latter gas is oxidised and converted into inodorous ducts. Thus, if charcoal be exposed to the action of air containing phuretted hydrogen gas, it condenses within its pores both this gas the atmospheric oxygen, which then converts the hydrogen into (HO) and the sulphur into sulphuric acid (SO_3).

The great porosity of wood charcoal is strikingly exhibited by attaching a pi lead to a stick of charcoal (fig. 53), so as to sink it in a cylinder of water, wh then placed under the receiver of the air-pump. On exhausting the air, innume bubbles will start from the pores of the charcoal, causing brisk effervescence. glass tube 10 or 12 inches long be thoroughly filled with ammonia gas (fig. 54) ported in a trough containing mercury, and a small stick of recently calcined

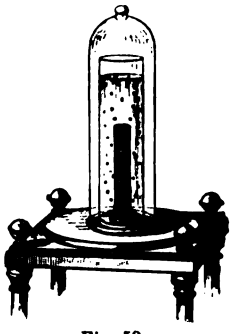


Fig. 53.

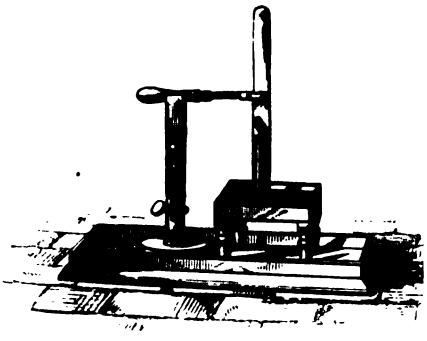


Fig. 54.

coal introduced through the mercury into the tube, the charcoal will absor ammonia so rapidly that the mercury will soon be forced up and fill the tube, car the charcoal up with it. On removing the charcoal, and placing it upon the a sensation of cold will be perceived from the rapid escape of ammonia, perce by its odour.

By exposing a fragment of recently calcined wood-charcoal under a jar filled hydrosulphuric acid gas for a few minutes, so that it may become saturated the gas, and then covering it with a jar of oxygen, the latter gas will act the former with such energy that the charcoal will burst into vivid combu The jar must not be closed air-tight at the bottom, or the sudden expansion burst it. Charcoal in powder exposed in a porcelain crucible may also be *ployed in the same* way. It should be pretty strongly heated in the covered

cible, and allowed to become nearly cool before being exposed to the hydrosulphuric acid.

Charcoal prepared from hard woods absorbs the largest volume of gas. Thus logwood charcoal has been found to absorb 111 times its volume of ammoniacal gas. Charcoal made from the shell of the cocoa-nut is even more absorbent, although its pores are quite invisible, and its fracture exhibits a semi-metallic lustre.

As the gases which are evolved in putrefaction are of a poisonous character, the power of wood charcoal to remove them acquires great practical importance, and is applied in very many cases; the charcoal in coarse powder is thickly strewn over matters from which the effluvium proceeds, or is exposed in shallow trays to the air to be sweetened, as in the wards of hospitals, &c. It has even been placed in a flat box of wire gauze to be fixed as a ventilator before a window through which the contaminated air might have access, and respirators constructed on the same principle have been found to afford protection against poisonous gases and vapours. The ventilating openings of sewers in the streets are also fitted with cases containing charcoal for the same purpose. Water is often filtered through charcoal in order to free it from the noxious and disagreeable sulphuretted hydrogen which is sometimes developed in it. For all such uses the charcoal should have been recently heated to redness in a covered vessel in order to expel the moisture which it attracts when exposed to the air, and the charcoal which has lost its power of absorption will be found to regain it in great measure when heated to redness.

This power of absorption which charcoal possesses is not confined to gases, for many liquid and solid substances are capable of being removed by that agent from their solution in water. This is most readily traced in the case of substances which impart a colour to the solution, such colour being often removed by the charcoal; if port wine or infusion of logwood be shaken with powdered charcoal (especially if the latter has been recently heated to redness in a closed crucible), the liquid, when filtered (fig. 55), will be found to have lost its colour; the colouring matter, however, seems merely to have adhered to the charcoal, for it may be extracted from the latter by treatment with a weak alkaline liquid.

Fig. 55.—Filtration.

The *decolorising power* of wood charcoal is very feeble in comparison with that possessed by *bone-black* or *animal charcoal*, which is obtained by heating bones in vessels from which the air is excluded. Bones are composed of about one-third of animal and two-thirds of mineral substances, the latter including phosphate of lime, which amounts to more than half the weight of the bone, and a little carbonate of lime. When bone is heated, as in a retort, so that air is not allowed to have free access to it, the anima[l] undergoes destructive distillation, its elements, carbon, hydr[ogen], and oxygen, assuming other forms, the greater part of th[em] nts, together with a portion of the carbon, escaping in [the] nd vaporous products, while a considerable proportion [re]s behind, intimately mixed with the earthy ingredi[ents] d *constituting the substance known as animal cha[rcoal]*.

ence between the products of the destructive distillation of bone and of wood deserves a passing notice. If a fragment of bone or a shaving of horn be heated in a glass tube closed at one end, the vapours which are evolved will be found strongly *alkaline* to test-papers, while those furnished by the wood were *acid;* this difference is to be ascribed mainly to the presence of nitrogen in the bone, wood being nearly free from that element; it will be found to hold good as a general rule, that the results of the destructive distillation of animal and vegetable matters containing much nitrogen are alkaline, from the presence of ammonia (NH_3) and similar compounds, while those furnished by non-nitrogenised substances possess acid characters: the peculiar odour which is emitted by the heated bone is characteristic, and affords us a test by which to distinguish roughly between nitrogenised and non-nitrogenised bodies.

An examination of the charred mass remaining as the ultimate result of the action of heat upon bone, shows it to contain much less carbon than that furnished by wood, for the bone-charcoal contains nearly nine-tenths of its weight of phosphate (with a little carbonate) of lime; the consequence of the presence of so large an amount of earthy matter must be to extend the particles of carbon over a larger space, and thus to expose a greater surface for the adhesion of colouring matters, &c. This may partly help to explain the very great superiority of bone-black to wood charcoal as a decolorising agent, and the explanation derives support from the circumstance that when animal charcoal is deprived of its earthy matter, for chemical uses, by washing with hydrochloric acid, its decolorising power is very considerably reduced. The application of this variety of charcoal is not confined to the chemical laboratory, but extends to manufacturing processes. The sugar-refiner decolorises his syrup by filtering it through a layer of animal charcoal, and the distiller employs charcoal to remove the empyreumatic oils with which distilled spirits are frequently contaminated.

Carbon is remarkable, among elementary bodies, for its indisposition to enter directly into combination with the other elements, whence it follows that most of the compounds of carbon have to be obtained by indirect processes. This element appears, indeed, to be incapable of uniting with any other at the ordinary temperature, and this circumstance is occasionally turned to useful account, as when the ends of wooden stakes are charred before being plunged into the earth, when the action of the atmospheric oxygen, which, in the presence of moisture, would be very active in effecting the decay of the wood, is resisted by the charcoal into which the external layer has been converted. The employment of black lead to protect metallic surfaces from rust is another application of the same principle. At a high temperature, however, carbon combines readily with oxygen, sulphur, and with some of the metals, and, at a very high temperature, even with hydrogen. The tendency of carbon to combine with oxygen under the influence of heat, is shown when a piece of charcoal is strongly heated at one point, when the carbon at this point at once combines with the oxygen of the surrounding air (forming carbonic acid), and the heat developed by this combustion raises the neighbouring particles of carbon to the temperature at which the element unites with oxygen, and thus the combustion is gradually propagated throughout the mass, which is ultimately converted entirely into carbonic acid gas, nothing remaining but the white ash, composed of the mineral substances *derived from the* wood employed for preparing the charcoal. It is worthy

of remark, that if charcoal had been a better conductor of heat, it would not have been so easily kindled, since the heat applied to any point of the mass would have been rapidly diffused over its whole bulk, and this point could not have attained the high temperature requisite for its ignition, until the whole mass had been heated nearly to the same degree; this is actually found to be the case in charcoal which has been very strongly heated (out of contact with air), when its conducting power is greatly improved, and it kindles with very great difficulty. The *calorific value* of carbon is represented by the number 8080, that is, 1 gr. of carbon, when burnt so as to form carbonic acid, is capable of raising 8080 grs. of water from 0° C. to 1° C.

A given weight of charcoal will produce twice as much available heat as an equal weight of wood, since the former contains more actual fuel and less oxygen, and much of the heat evolved by the wood is absorbed or rendered latent in the steam and other vapours which are produced by the action of heat upon it. The attraction possessed by carbon for oxygen at a high temperature is turned to account in metallurgic operations, when coal and charcoal are employed for extracting the metals from their compounds with oxygen.*

The unchangeable solidity of carbon is another remarkable feature. It is stated that some approach has been made, at extremely high temperatures, to the fusion and vaporisation of carbon, but it cannot be said to have been fairly established that this element is able to exist in any other than the solid form. Nor can any substance be found by the aid of which carbon may be brought into the liquid form by the process of solution, for although charcoal gradually disappears when boiled with sulphuric and nitric acids, it does not undergo a simple solution, but is converted, as will be seen hereafter, into carbonic acid.

52. Coal.—The various substances which are classed together under the name of coal are characterised by the presence of carbon as a largely predominant constituent, associated with smaller quantities of hydrogen, oxygen, nitrogen, sulphur, and certain mineral matters which compose the ash. Coal appears to have been formed by a peculiar decomposition or fermentation of buried vegetable matter, resulting in the separation of a large proportion of its hydrogen in the form of marsh-gas (C_2H_4), and similar compounds, and of its oxygen in the form of carbonic acid (CO_2), the carbon accumulating in the residue. Thus, cellulose ($C_{12}H_{10}O_{10}$), which constitutes the bulk of woody fibre, might be imagined to decompose according to the equation $2C_{12}H_{10}O_{10} = 5C_2H_4 + 10\,CO_2 + C_4$, and the occurrence of marsh-gas, and of the petroleum hydrocarbons of similar composition, as well as of carbonic acid, in connexion with deposits of coal, supports this account of its formation. Marsh-gas and carbonic acid are the ordinary products of the fermentation of vegetable matter, and a spontaneous carbonisation is often witnessed in the "heating" of damp hay. But just as the action of heat upon wood produces a charcoal containing small quantities of the other organic elements, so the carbonising process by which the plants have been transformed into coal, has left behind some of the hydrogen, oxygen, and nitrogen; the last, as well probably as a little of the sulphur, having been derived from the vegetable albumen and similar substances which are always present in plants. The

* Easily reducible oxides, such as oxide of lead, give carbonic acid when heated w charcoal; $2PbO + C = Pb_2 + CO_2$, but oxides which are not easily reducible, su *oxide of zinc, give carbonic oxide*; $ZnO + C = CO + Zn$.

chief part of the sulphur is generally present in the form of iron pyrites, derived from some extraneous source. The examination of a peat-bog is very instructive with reference to the formation of coal, as affording examples of vegetable matter in every stage of decomposition, from that in which the organised structure is still clearly visible, to the black carbonaceous mass which only requires consolidation by pressure in order to resemble a true coal.

The three principal varieties of coal—*lignite*, *bituminous coal*, and *anthracite*—present us with the material in different stages of carbonisation; the lignite, or brown coal, presenting indications of organised structure, and containing considerable proportions of hydrogen and oxygen, while anthracite often contains little else than carbon and the mineral matter or ash. The following table shows the progressive diminution in the proportions of hydrogen and oxygen in the passage from wood to anthracite :—

	Carbon.	Hydrogen.	Oxygen.
Wood, ...	100	12·18	88·07
Peat, ...	100	9·85	55·67
Lignite, ...	100	8·37	42·42
Bituminous coal, . .	100	6·12	21·28
Anthracite, . . .	100	2·84	1·74

The combustion of coal is a somewhat complex process, in consequence of the re-arrangement which its elements undergo when the coal is subjected to the action of heat.

As soon as a flame is applied to kindle the coal, the heated portion undergoes destructive distillation, evolving various combustible gases and vapours, which take fire and convey the heat to remoter portions of the coal. Whilst the elements of the exterior portion of coal are undergoing combustion, the heat thus evolved is submitting the interior of the mass to destructive distillation, resulting in the production of various compounds of carbon and hydrogen. Some of these products, such as marsh-gas (C_2H_4) and olefiant gas (C_4H_4), burn without smoke; while others, like benzole ($C_{12}H_6$) and naphthaline ($C_{20}H_8$), which contain a very large proportion of carbon, undergo partial combustion, and a considerable quantity of carbon, not meeting with enough heated oxygen in the vicinity to burn it entirely, escapes in a very finely divided state as smoke or soot, which is deposited in the chimney, mixed with a little carbonate of ammonia, and small quantities of other products of the distillation of coal. When the gas has been expelled from the coal, there remains a mass of coke or cinder, which burns with a steady glow until the whole of its carbon is consumed, and leaves an *ash*, consisting of the mineral substances present in the coal. The final results of the perfect combustion of coal would be carbonic acid (CO_2), water (HO), nitrogen, a little sulphurous acid (SO_2), and ash. The production of smoke in a furnace supplied with coal may be prevented by charging the coal in small quantities at a time in front of the fire, so that the highly carbonaceous vapours must come in contact with a large volume of heated air before reaching the chimney. In arrangements for consuming the smoke, hot air is judiciously admitted at the back of the fire, in order to meet and consume the heated carbonaceous particles before they pass into the chimney.

The difference in the composition of the several varieties of coal gives *to a great* difference in their mode of burning.

The following table exhibits the composition of representative specimens of the three principal varieties :—

Composition of Coal.

	Lignite.	Bituminous Coal.	Anthracite.
Carbon, ...	66·32	78·57	90·39
Hydrogen, . . .	5·63	5·29	3·28
Nitrogen, . . .	0·56	1·84	0·83
Oxygen, ...	22·86	12·88	2·98
Sulphur, ...	2·36	0·39	0·91
Ash,*	2·27	1·03	1·61
	100·00	100·00	100·00

The lignites furnish a much larger quantity of gas under the action of heat, and therefore burn with more flame than the other varieties, leaving a coke which retains the form of the original coal; while bituminous coal softens and cakes together,—a useful property, since it allows even the dust of such coal to be burnt, if the fire be judiciously managed. Anthracite (*stone coal* or *Welsh coal*) is much less easily combustible than either of the others, and since it yields but little gas when heated, it usually burns with little flame or smoke. This variety of coal is so compact that it will not usually burn in ordinary grates, but is much employed for furnaces.

53. Carbon is capable of combining with oxygen in two proportions, forming the compounds known as *carbonic oxide* and *carbonic acid*, the composition of which is shown in the following table :—

Oxides of Carbon.

		Parts by weight.	
		C	O
Carbonic oxide, . . .	CO,	6	8
Carbonic acid, . . .	CO_2,	6	16

Carbonic Acid.

54. It has been already mentioned that carbonic acid is a component of the atmosphere, which usually contains about four volumes of carbonic acid in 10,000 volumes of air. This carbonic acid is chiefly formed by the operation of the atmospheric oxygen in supporting combustion and respiration.

All substances used as fuel contain a large proportion of carbon, which, in the act of combustion, combines with the oxygen, and escapes into the atmosphere in the form of carbonic acid.

In the process of respiration, the carbonic acid is formed from the carbon contained in the different portions of the animal frame to which oxygen is conveyed by the blood, having been taken up by the latter in passing through the lungs, where it gives out, in exchange for the oxygen, a quantity of carbonic acid produced by the union of a former supply of oxygen with the carbon of the different organs to which the blood is supplied, and which, as they are constantly corroded and destroyed by this oxidising action of the blood, are repaired by the supply of food taken into the body. This conversion of the carbon of the organs into carbonic acid will be again referred to; it will be at once evident that it must be concerned in the maintenance of the animal heat.

* *The ash of coal consists chiefly of silica*, alumina, and peroxide of iron.

The leaves of plants, under the influence of light, have the power of decomposing the carbonic acid of the atmosphere, the carbon of which is applied to the production of vegetable compounds forming portions of the organism of the plant, and when this dies, the carbon is restored, after a lapse of time more or less considerable, to the atmosphere, in the same form, namely, that of carbonic acid, in which it originally existed there. If the plant should have been consumed as food by animals, its carbon will have been eventually converted into carbonic acid by respiration; the use of the plant as fuel, either soon after its death (wood), or after the lapse of time has converted it into coal, will also consign its carbon to the air in the form of carbonic acid. Even if the plant be left to *decay*, this process involves a slow conversion of its carbon into carbonic acid by the oxygen of the air.*

Putrefaction and *fermentation* are also very important processes concerned in restoring to the air, in the form of carbonic acid, the carbon contained in dead vegetable and animal matter. Although, in a popular sense, these two processes are distinct, yet their chemical operation is of the same kind, consisting in *the resolution of a complex substance into simpler forms, produced by contact with some other substance in a state of chemical change.* The discussion of the true nature of the process (which is even now somewhat obscure) would be premature at this stage, and it will suffice for the present to state that carbonic acid is one of the simpler forms into which the carbon is converted by the metamorphosis which ensues so quickly upon the death of animals and vegetables.

The production of carbonic acid in combustion, respiration, and fermentation may be very easily proved by experiment. If a dry bottle be placed over a burning wax taper standing on the table, the sides of the bottle will be covered with dew from the combustion of the hydrogen in the wax; and if a little clear lime-water be shaken in the bottle, the milky deposit of carbonate of lime will indicate the formation of carbonic acid.

By arranging two bottles, as represented in fig. 56, and inspiring through the tube A, air will bubble through the lime-water in B, before entering the lungs, and will then be found to contain too little carbonic acid to produce a milkiness, but on expiring the air it will bubble through C, and will render the lime-water in this bottle very distinctly turbid.

Fig. 56.

If a little sugar be dissolved in eight or ten times its weight of warm (not hot) water, in the flask A (fig. 57), and a little dried yeast previously rubbed down with water added, fermentation will commence in the course of an hour or less, and carbonic acid may be collected in the jar B.

55. In the mineral kingdom, free carbonic acid is pretty abundant. The gas issues from the earth in some places in considerable quantity, as at Nauheim, where there is said to be a spring exhaling about 1,000,000 lbs. of the gas annually. Many spring waters, those of Seltzer and Pyrmont, for example, are very highly charged with the gas.

* In the dark, according to Boussingault, plants evolve carbonic acid. He found that a square metre (39·37 sq. inches) of oleander leaves decomposed, in sunlight, on an average, 1·108 litre (67·6 cubic inches) of carbonic acid every hour; whilst the same extent of leaf, in the dark, emitted 0·07 litre (4·27 cubic inches) of carbonic acid in the hour. Even under the influence of light, flowers have been found to absorb oxygen and evolve carbonic acid.

But it occurs in far larger quantity in a state of combination with lime, forming the immense deposits of *limestone*, marble, and chalk, which compose so large a portion of the crust of the globe. Carbonate of lime is also met with in the animal kingdom. Fish shells and pearls contain about two-thirds of their weight of this substance, whilst egg-shells contain as much as nine-tenths of carbonate of lime.

Fig. 57.

The expulsion of the carbonic acid from limestone ($CaO.CO_2$) forms the object of the process of *lime burning*, by which the large supply of lime (CaO) is obtained for building and other purposes. But if it be required to obtain the carbonic acid without regard to the lime, it is better to decompose the carbonate of lime with an acid.

Preparation of carbonic acid.—The form of the carbonate of lime, and the nature of the acid employed, are by no means matters of indifference. If dilute sulphuric acid be poured upon fragments of marble, the effervescence which occurs at first soon ceases, for the surface of the marble becomes coated with the nearly insoluble sulphate of lime, by which it is protected from the further action of the acid—

$$\underset{\text{Marble.}}{CaO.CO_2} + \underset{\text{Sulphuric acid.}}{HO.SO_3} = \underset{\text{Sulphate of lime.}}{CaO.SO_3} + HO + CO_2$$

if the marble be finely powdered, or if powdered chalk be employed, each particle of the carbonate of lime will be acted upon. When lumps of carbonate of lime are acted upon by hydrochloric acid, there is no danger that any will escape the action of the acid, for the chloride of calcium produced is one of the most soluble salts—

$$\underset{\text{Marble.}}{CaO.CO_2} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Chloride of calcium.}}{CaCl} + HO + CO_2.$$

For the ordinary purposes of experiment, carbonic acid is most easily obtained by the action of diluted hydrochloric acid upon small fragments of marble (fig. 58), the latter being covered with water, and hydrochloric acid poured in through the funnel-tube. The gas may be collected by downward displacement.

Fig. 58.—Preparation of carbonic acid.

56. *Properties of carbonic acid.*—Carbonic acid gas is invisible, like the gases already examined, but is distinguished by a peculiar pungent odour, as is perceived in *soda-water*. *It is more than half as heavy* again as atmospheric air,

its specific gravity being 1·529, which causes its accumulation near the floor of such confined spaces as the Grotto del Cane, where it issues from fissures in the rock.

The high specific gravity of carbonic acid may be shown by pouring it into a light jar attached to a balance, and counterpoised by a weight in the opposite scale (fig. 59).

Fig. 59.

Another favourite illustration consists in floating a soap-bubble on the surface of a layer of the gas generated in the large jar (fig. 60), by pouring diluted sulphuric acid upon a few ounces of chalk made into a thin cream with water.

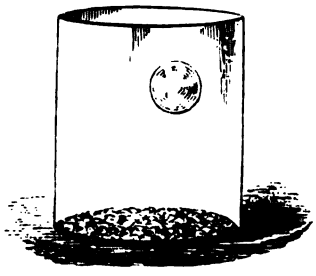


Fig. 60.

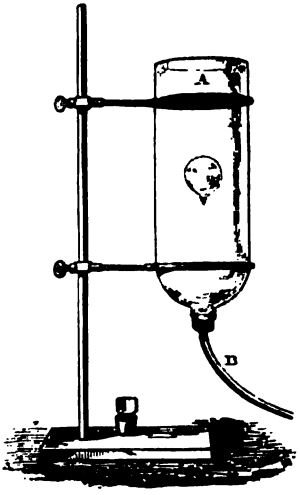


Fig. 61.

If a small balloon, made of collodion be placed in the jar A (fig. 61), it will ascend *on the admission of* carbonic acid through the tube B.

The power which carbonic acid possesses of extinguishing flame is y important, and has received practical application in the case of burn- mines which must otherwise have n flooded with water.* Many at- npts have also been made from time time to employ this gas for subdu- ordinary conflagrations, but their ccess has hitherto been very partial. will be remembered that pure nitro- n is also capable of extinguishing flame of a taper, but a large pro- rtion of this gas may be present in without affecting the flame, whereas aper is extinguished in air contain- g one-eighth of its volume of car- nic acid, and is sensibly diminished brilliancy by a much smaller pro- rtion of the gas.

Fig. 62.

The power of extinguishing flame, con- ed with the high density of carbonic d, admit of some very interesting illus- tions.

Carbonic acid may be poured from some distance upon a candle, and will extin- ish it at once.

A large torch of blazing tow may be plunged beneath the surface of the carbonic id in the jar, fig. 60.

Carbonic acid may be raised in a glass bucket (fig. 62) from a large jar, and ured into another jar the air in which has been eviously tested with a taper.

A wire stand with several tapers fixed at different els may be placed in the jar A, fig. 63, and car- nic acid gradually admitted through a flexible be connected with the neck of the jar, from the tern B, a hole in the cover of which allows air enter it as the gas flows out; the flame of each per will gradually expire as the surface of the car- nic acid rises in the jar.

Fig. 63.

A jar of oxygen may be placed over a jar of car- nic acid, as shown in fig. 15, and a taper let down rough the oxygen, in which it will burn bril- ntly, into the carbonic acid, which extinguishes and if it be quickly raised again into the oxygen, will rekindle with a slight detonation. This al- nate extinction and rekindling may be repeated veral times.

On account of this extinguishing power of rbonic acid, a taper cannot continue to burn a confined portion of air until it has ex- usted the oxygen, but only until its combustion has produced a suffi- nt quantity of carbonic acid to extinguish the flame.

To demonstrate this, advantage may be taken of the circumstance that phos- rus will continue to burn in spite of the presence of carbonic acid. Upon the nd A (fig. 64) a small piece of phosphorus is placed, and a taper is attached

* All gases which take no part in combustion may extinguish flame, even in the sense of air, by absorbing heat and reducing the temperature below the burning- nt.

to the stand by a wire. The cork B fits air-tight into the jar, a
of copper wire bent so that it may be heated by the flame of th
water is poured into the plate to pre
of any fresh air. If the taper be kin
placed over it, the flame will soon die
ing the jar so that the hot wire may
phorus, its combustion will show th
amount of oxygen still remains.

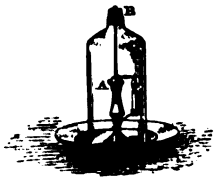


Fig 64.

In the same manner, an animal
confined portion of air only until
it with so much carbonic acid t
effect of this gas begins to be felt,
quantity of oxygen still remaining.

If the air contained in the jar A (fig. 65) standing over wate
or three times through the tube B, a painful sense of oppression w
consequence of the accu
bonic acid. By immersi
spoon C, containing a piec
phorus, and having a light
it may be shown that
is enough carbonic acid
taper, the oxygen is not
phosphorus continues to b

Fig. 65.

Carbonic acid is not
taken into the stomach
injuriously when breat
an obstacle to that esc
acid, by diffusion, fro
the venous circulation
and its consequent rep
oxygen necessary to
Any hindrance to t
must impede respirat
hindrance would, of co
by carbonic acid pre
inhaled, in proportion to its quantity. The difference in c
temperament in individuals, makes it impossible that an
rule should be laid down as to the precise quantity of
which may be present in air without injury to respiration,
safely asserted that it is not advisable to breathe for any
in air containing more than $\frac{1}{1000}$th (0·1 per cent.) of its
bonic acid.

There appears to be no immediate danger, however, un
acid amounts to $\frac{1}{200}$th (0·5 per cent.), when most persons
the languor and headache attending the action of this gas.
portion of carbonic acid produces insensibility, and air con
its volume of carbonic acid causes suffocation. The danger
wells, cellars, and other confined places, is due to the a
this gas, either exhaled from the earth or produced by d
matter. The ordinary test applied to such confined air b
candle is only to be depended upon if the candle burns as
confined space as in the external air; should the flame bec
would be unsafe to enter, for experience has shown th
y continue for some time in an atmosphere dangerousl
bonic acid.

accidents from *choke damp* and *after damp* in coal mines, and e accumulation in brewers' and distillers' vats of the carbonic acid g from fermentation, are also examples of the fatal effect of this

ir issuing from the lungs of a man at each expiration contains to 4 volumes of carbonic acid in 100 volumes of air, and could not, e, be breathed again without danger. The total amount of car- id evolved by the lungs and skin amounts to about 0·7 cubic foot r. In order that it may be breathed again without inconvenience ould be distributed through 140 cubic feet of fresh air, or a easuring 5·2 feet each way. Hence the necessity for a constant f fresh air by ventilation, to dilute the carbonic acid to such an hat it may cease to impede respiration. This becomes the more y where an additional quantity of carbonic acid is supplied by or gas-lights. Two ordinary gas-burners, each consuming three et of gas per hour, will produce as much carbonic acid as one man. dly, a natural provision for ventilation exists in the circumstance processes of respiration and combustion, which contaminate the raise its temperature, thus diminishing its specific gravity by m, and causing it to ascend e place to fresh air. Hence ated air always accumulates ceiling of an apartment, and es necessary to afford it an by opening the upper sash of dow, since the chimney ven- immediately only the lower the room.

Fig. 66.

principles may be illustrated by y simple experiments. quart jars (fig. 66) are filled with acid, and after being tested with ed in flask is lowered into each, one flask containing cold and the other er. After a few minutes, the jar with the cold flask will still contain enough acid to extinguish the taper, whilst the air in r will support combustion brilliantly.

A tapered glass jar (fig. 67) is placed over a stand, three lighted tapers are fixed at different The vitiated air, rising to the top of the jar, extinguishes the uppermost taper first, and the others By quickly removing the stopper and a little before the lowest taper has expired, will be ventilated and the taper revived.

Fig. 67.

A jar (fig. 68), with a glass chimney fixed into through a cork or piece of vulcanised tubing, is stand with two tapers, one of which is near the jar, and the other beneath the aperture chimney. If a crevice for the entrance of air be between the jar and the table, the lower taper will burn indefinitely, whilst the upper one will extinguished by the carbonic acid accumulating

apartments, the incidental crevices of the doors and windows upon for the entrance of fresh air, whilst the contaminated out by the chimney, but in large buildings special provision for the *two air currents*. *In mines* this becomes the more

necessary, since the air receives much additional contamination gases (marsh-gas and carbonic acid) evolved from the workings, the smoke occasioned in blasting with gun Mines are generally provided with two sh ventilation, under one of which (the *upcas* a fire is maintained to produce the upward which carries off the foul air, whilst the fi descends by the other (*downcast* shaft). T rent of fresh air is forced by wooden parti divide itself, and pass through every portio workings.

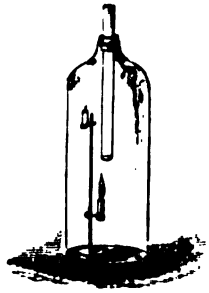


Fig. 68.

The operation of such provisions for ventilation exhibited.

A tall jar (fig. 69) is fitted with a ring of cork, a wide glass chimney (A). If this be placed ove standing in a plate of water, the accumulation of air will soon extinguish the taper; but if a second (B), supported in a wire ring, be placed within the wide chimney, fresh enter through the interval between the two, and the smoke from a piece paper will demonstrate the existence of the two currents, as shown by the a

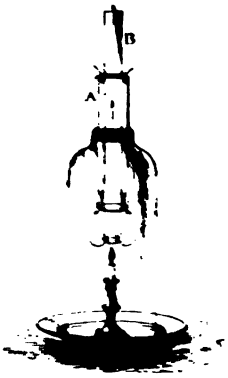


Fig. 69.

A small box (fig. 70) is provided with a glass at each end. In one of these (B), representing t shaft, a lighted taper is suspended. A piece of brown paper may be held in each chimney to direction of the current. On closing A with plate, the taper in B will be extinguished, the of fresh air being prevented. By breathing ge A the taper will also be extinguished. The ex may be varied by pouring carbonic acid and alternately into A, when the taper will be exti and rekindled by turns.

A pint bell-jar (fig. 71) is placed over a taper in a tray of water. If a chimney (a common lar be placed on the top of the jar, the flame of will gradually die out, because no provision the establishment of the two currents, but on a piece of tin-plate or card-board into the chi as to divide it, the taper will be revived, and t from the brown paper will distinguish the upcast downcast shaft.

If a little water be poured into a wide-mouthed bottle of acid, and the bottle be then firmly closed by the palm of the will be found, on shaking th violently, that the carbonic absorbed, and the palm of th is sucked into the bottle. T

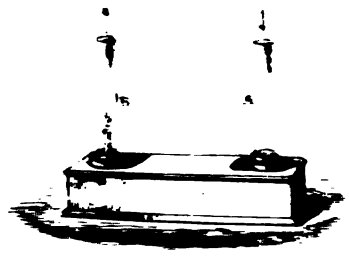
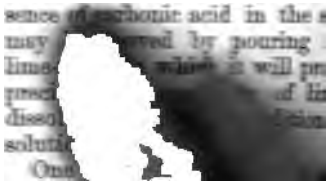


Fig. 71.

ordinary pressure of the air gas, equa in weight to near vessel, under a pressu



carb

sphere—that is, if twice or thrice the quantity of carbonic acid be compressed into the same space, the water will still dissolve one pint of the gas, but the weight of this pint will now be twice or thrice that of the pint of uncompressed gas, so that the water will have dissolved 32 or 48 grains of the gas, accordingly as the pressure had been doubled or trebled. As soon, however, as the pressure is removed, the compressed carbonic acid will resume its former state, with the exception of that portion which the water is capable of retaining in solution under the ordinary pressure of the atmosphere. Thus, if the water had been charged with carbonic acid under a pressure equal to thrice that of the atmosphere, and had therefore absorbed 48 grains of the gas, it would only retain 16 grains when the pressure was taken off, allowing 32 grains to escape in minute bubbles, producing the appearance known as *effervescence*. This affords an explanation of the properties of soda-water, which is prepared by charging water with carbonic acid gas under considerable pressure, and rapidly confining it in strong bottles. As soon as the resistance offered by the cork to the expansion of the gas is removed, the excess of the carbonic acid, above that which it can hold in solution at the ordinary pressure of the air, escapes with effervescence. In a similar manner, the waters of certain springs become charged with carbonic acid, under high pressure, beneath the surface of the earth, and when, upon their rising to the surface, this pressure is removed, the excess of carbonic acid escapes with effervescence, giving rise to the sparkling appearance and sharp flavour which renders spring water so agreeable. On the other hand, the waters of lakes and rivers are usually flat and insipid, because they hold in solution so small a quantity of uncombined carbonic acid.

Fig. 71.

The sparkling character of champagne, bottled beer, &c., is due to the presence in these liquids of a quantity of carbonic acid which has been generated by fermentation, subsequent to bottling, and has therefore been retained in the liquid under pressure. In the case of Seidlitz powders and soda-water powders, the effervescence caused by dissolving them in water is due to the disengagement of carbonic acid, caused by the action of the tartaric acid, which composes one of the powders, upon the bicarbonate of soda, producing tartrate of soda and carbonic acid gas. In the dry state these powders may be mixed without any chemical change, but the addition of water immediately causes the effervescence.

The solubility of carbonic acid in water is of great importance in the chemistry of nature; for this acid, brought down from the atmosphere dissolved in rain, is able to act chemically upon rocks, such as granite, containing alkalies—the carbonic acid combining with these, and thus disintegrating or crumbling down the rock, an effect much assisted by the mechanical action of the expansion of freezing water in the interstices. It is [illegible] that soils are thus formed by the slow decomposition of rocks, and [illegible] these soils are capable of supporting vegetation [illegible] of [illegible] is again of service, not only as a supplying [illegible] carbon through its roots, but as [illegible] mineral food of the plant (such as

phosphate of lime), which pure water could not dissolve, and which the plant cannot take up except in the dissolved state.

57. Although carbonic acid retains its state of gas under all temperatures and pressures to which it is commonly exposed, it is capable of assuming the liquid and even the solid state.

When exposed to a pressure of 38·5 atmospheres (577·5 lbs. upon the square inch) at 32° F., carbonic acid condenses to a colourless liquid of sp. gr. 0·83 (water = 1), and at a temperature of —70° F. (70° below the zero, or 102° below the freezing point, F.), becomes a transparent mass of solid carbonic acid resembling ice.

A small specimen of liquid carbonic acid is easily prepared. A strong tube of green glass (A, fig. 72) is selected, about 12 inches long, $\frac{1}{4}$ inch diameter in the bore, and $\frac{1}{3}$ inch thick in the walls. With the aid of the blowpipe flame this tube is softened and drawn off at about an inch from one end, as at B, which is thus closed (C). This operation should be performed slowly in order that the closed end may not be much thinner than the walls of the tube. When the tube has cooled, between 30 and 40 grs. of powdered bicarbonate of ammonia (ordinary sesquicarbonate which has crumbled down) are tightly rammed into it with a glass rod. This part of the tube is then surrounded with a few folds of wet blotting-paper to keep it cool, and the tube is bent, just beyond the carbonate of ammonia, to a somewhat obtuse angle (D). The tube is then softened at about an inch from the open

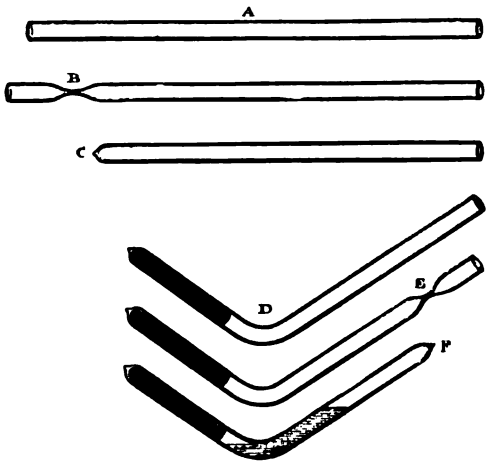


Fig. 72.

end, and drawn out to a narrow neck (E), through which a measured drachm of oil of vitriol is poured down a funnel-tube, so as not to soil the neck which is then carefully drawn out and sealed by the blowpipe flame, as at F. The empty space in the tube should not exceed $\frac{1}{8}$ cubic inch.

When the tube is thoroughly cold, it is suspended by strings in such a position that the operator, having retired behind a screen at some distance, may reverse the tube, allowing the acid to flow into the limb containing the carbonate of ammonia; or the tube may be fixed in a box which is shut up, and reversed as to bring the tube into the required position.

If the tube be strong enough to resist the pressure, it will after hours, that a layer of liquid carbonic acid has been formed above solution of sulphate of ammonia. By cooling the empty limb pounded ice and salt, or of hydrochloric acid and sulphate of can be made to distil itself over into this limb, leaving the sulphate the other.

On a larger scale the gas is liquefied and is employed for illustrating the laws of heat to escape into the air, the evaporation of which solidify the remainder, which becomes a solid exposed to air, with production of intense cold. Carbonic acid with ether forms one of the most powerful freezing mixtures in the liquefaction and solidification of gases.

Carbonic acid may be separated

lrate of potash, which absorbs it, forming carbonate of potash. on of carbonic acid is inferred either from the diminution in red by the gas when treated with potash, or from the increase the latter.

er case the gas is carefully measured over mercury (fig. 73), with due mperature and barometric pressure, and a little concentrated solution rown up through a curved inge, introduced into the ube beneath the surface of The tube is gently shaken nds to promote the absorp-, and, after a few minutes' inution of volume is read of solution of potash, damp otash in the solid state is troduced, in the form of r balls attached to a wire. the weight of carbonic eous mixture, the latter is h a bulb-apparatus (C, fig. g a strong solution of po- ghed before and after the e gas. When the propor- ic acid in the gas is small, attach to the bulb-appara- e, containing solid hydrate chloride of calcium, or moistened with sulphuric purpose of retaining any er which the large volume of unabsorbed gas might carry away in gh the solution of potash.

Fig. 73.

ate organic analysis.—It is necessary to determine in this weight of carbonic acid, in order to ascertain the proportion of ent in organic substances. For this purpose, an accurately ntity (usually from seven to ten grains) of the organic substance fully mixed with some compound from which it can obtain high temperature, such as oxide of copper (CuO) or chromate $O.CrO_3$), care being taken to employ a large excess of the gent. The mixture is introduced into a *combustion-tube* of ss (which is free from lead and noted for its infusibility) of the in A, fig. 74. This tube is provided with a small tube B,

paratus for organ s.

ich is conn a tube of caoutchouc dually he tube in a charcoal

furnace, or over a properly constructed gas-burner, the hydrogen and c contained in the organic substance are converted, respectively, into and carbonic acid, by the oxygen derived from the chromate of lead or of copper. The water is absorbed by the chloride of calcium in B, a increase of weight in this tube will indicate the quantity of water f in the combustion, whilst that of the potash bulbs will show the w of the carbonic acid. When the whole length of the tube is red ho no more gas passes through the bulbs, the sealed point D of the t broken off, and air drawn through by applying suction at E, in or sweep out the last traces of water and carbonic acid into the chlor calcium and potash. Sometimes the organic substance is heated in a platinum tray, placed within a glass tube, through which a stream o oxygen is passed, the products of combustion being afterwards m pass over red-hot oxide of copper, to convert any carbonic oxide int bonic acid, and collected for weighing as before.

When the organic substance contains carbon, hydrogen, and ox the weight of this last is inferred by subtracting the weights of the c and hydrogen from that of the substance. As an example of the *ult analysis of an organic substance*, the results of an analysis of oxali are here given—

10 grs. of oxalic acid, dried at 212° F., gave 9·78 grs. of carboni and 2·00 grs of water.

$$\begin{array}{cccccc} CO_2 & & C & & CO_2 & \\ 22 & : & 6 & :: & 9{\cdot}78 & : x \end{array}$$

$x = 2{\cdot}67$ grs. of carbon in 10 grs. of oxalic acid.

$$\begin{array}{cccccc} HO & & H & & HO & \\ 9 & : & 1 & :: & 2{\cdot}00 & : y \end{array}$$

$y = 0{\cdot}22$ gr. of hydrogen in 10 grs. of oxalic acid.

It having been ascertained by preliminary experiments that oxali contains only carbon, hydrogen, and oxygen, 10 (oxalic acid) *minus* (carbon and hydrogen) = 7·11 grs. of oxygen in 10 grs. of oxalic acid

It appears, therefore, that

10 grs. of oxalic acid contain
2·67 „ carbon,
0·22 „ hydrogen, and
7·11 „ oxygen.

Empirical and rational formulæ.—In order to deduce from numbers the chemical formula for oxalic acid, that is, the formula ex ing the number of combining weights of each element, it will be nece of course, to divide the weight of each element by the number repr ing its combining weight in the table at p. 2.

Thus $\frac{2{\cdot}67}{6} = 0{\cdot}44$ of a combining weight of carbon;

$\frac{0{\cdot}22}{1} = 0{\cdot}22$ „ „ hydrogen;

$\frac{7{\cdot}11}{8} = 0{\cdot}88$ „ „ oxygen.

And the formula of oxalic acid might be written $C_{44}H_{22}O_{88}$. But as fractions are not admissible in such a formula, it would be written $C_2H_1O_8$. This, however, is only an *empirical* formula for oxalic acid, that is, a formula which represents its *composition* only, without reference to its *constitution*, *i.e.*, to the absolute number of combining weights present, and to the mode in which they are grouped or arranged within the compound. A formula professing to give such information would be termed a *rational* formula, and can only be arrived at by the careful study of the relation of the substance under examination to others of which the combining weights are certainly known. Thus, it is found that one combining weight (47 parts) of potash requires 45 parts of dry oxalic acid to neutralise it and form the oxalate of potash. Hence it is reasonable to regard 45 as the combining weight of dry oxalic acid. Since the above analysis has proved this quantity of oxalic acid to contain 12 (two combining weights) of carbon, 1 (one combining weight) of hydrogen, and 32 (four combining weights) of oxygen, the formula would be written C_2HO_4. In determining whether this formula represents only one grouping of the elements, or whether it contains two or more groups in combination, the chemist is guided by the results of a more minute study of the decompositions which the compound undergoes under varied conditions.

60. *Salts formed by carbonic acid.*—Although so ready to combine with the alkalies and alkaline earths (as shown in its absorption by solution of potash and by lime-water), carbonic acid must be classed among the weaker acids. It does not neutralise the alkalies completely, and it may be displaced from its combinations with bases by most other acids. Its action upon the colouring matter of litmus is feeble and transient. If a solution of carbonic acid in water be added to blue infusion of litmus, a wine-red liquid is produced, which becomes blue again when boiled, losing its carbonic acid; whilst litmus reddened by sulphuric, hydrochloric, or nitric acid, acquires a brighter red colour, which is permanent on boiling.

With each of the alkalies carbonic acid forms two well-defined salts, the *carbonate* and *bicarbonate*. Thus, the carbonates of potash and soda are represented by the formulæ, $KO.CO_2$ and $NaO.CO_2$, whilst the bicarbonates are $KO.HO.2CO_2$ and $NaO.HO.2CO_2$. The existence of the latter salts would favour the belief in the existence of a hydrate of carbonic acid ($HO.CO_2$), when they would become

$$KO.CO_2, HO.CO_2 \text{ and } NaO.CO_2, HO.CO_2,$$

although no such combination of water with carbonic acid has yet been obtained in the separate state. Perfectly dry carbonic acid gas is not absorbed by pure quicklime (CaO), but when a little water is added combination at once takes place. This supports the view entertained by some chemists, that CO_2 is not an acid until it is associated with water, and they therefore speak of it as *carbonic anhydride*, reserving the name carbonic acid for the as yet undiscovered compound $HO.CO_2$ (or HCO_3).

The following are some of the principal carbonates which are found in nature or employed in the arts :—

Chemical Name.	Common Name.	Equivalent Formula.	Atomic Unitary Formula.
Carbonate of potash	Potashes, pearl-ash	$KO . CO_2$	$K_2C\Theta_3$
Bicarbonate of potash		$KO . HO . 2CO_2$	$KH . C\Theta_3$
Carbonate of soda	Alkali Washing soda	$NaO . CO_2$	$Na_2C\Theta_3$
Bicarbonate of soda	Carbonate of soda	$NaO . HO . 2CO_2$	$NaHC\Theta_3$
Bicarbonate of ammonia	Smelling salts Preston salts Carbonate of ammonia	$2NH_3 . 2HO . 3CO_2$	$2[(H_4N)_2C\Theta_3]C\Theta_2$
Carbonate of lime	Limestone, chalk Marble	$CaO . CO_2$	$CaC\Theta_3$
Basic carbonate of magnesia	*Magnesia alba* Magnesia	$3(MgO . CO_2)$, $MgO . HO$.	$3MgC\Theta_3 . MgH_2\Theta_2$
Carbonate of iron	Spathic iron ore	$FeO . CO_2$	$FeC\Theta_3$
Carbonate of zinc	Calamine	$ZnO . CO_2$	$ZnC\Theta_3$
Basic carbonate of copper	Malachite	$CuO . CO_2$, $CuO . HO$	$CuC\Theta_3 . H_2\Theta . CuC\Theta_3$
Basic carbonate of lead	White lead	$2(PbO . CO_2)$, $PbO . HO$	$2PbC\Theta_3 . Pb\Theta . H_2\Theta$
Double carbonate of lime and magnesia	Dolomite Magnesian limestone	$CaO . MgO . 2CO_2$	$MgCa\,2C\Theta_3$

proof of the composition of carbonic acid.—Lavoisier appears to have ... to prove that carbonic acid was formed when carbon combined with ... composition was first analytically demonstrated by Smithson Tennant ... carbonate of lime with phosphorus in a sealed glass tube, and ... of lime and carbon, the latter having parted with its oxygen to ... phosphorus into phosphoric acid.

It hav... method of demonstrating the composition of carbonic acid consists in ... contains ... of potassium into a bulb tube, through which a current of car... (carbon a... by passing through oil of vitriol, or over chloride of calcium) is ... It appe... the heat of a spirit-lamp to the bulb; the metal will soon ... it robs of its oxygen, leaving the carbon as a black mass upon ... potash produced by the oxidation of the potassium enters ... other portion of the carbonic acid, forming a white mass of ... $K_2 = 2(KO . CO_2) + C$. If slices of sodium be ar... nate layers with dried chalk (carbonate of lime), and ... mp, vivid combustion will ensue, and much carbon ... $Na_2 = CaO + 2NaO + C$).

Empirical ... metals, however, which are not endowed ... numbers the c... oxygen, do not carry the decomposition ... ing the number ... us, iron and zinc* at a ... h tempera... of course, to div... lf of its oxygen, a re... ich may ... ing its combinin... rbon itself. If a... filled ... luess in a furn... and ... it will be foun... ing ... of the tube, ...

Thus ...

$$\frac{0}{7{\cdot}1} \quad \frac{\cdot}{8}$$

ger the properties of carbonic acid, but that, on the approach of a taper, akes fire, and burns with a beautiful blue lambent flame, similar to that ich is often observed to play over the surface of a clear fire. Both nes, in fact, are due to the same gas, and in both cases this gas results

Fig. 75.

m the same chemical change, for in the tube the carbonic acid yields lf of its oxygen to the charcoal, both becoming converted into carbonic ide; $CO_2 + C = 2CO$. In the fire, the carbonic acid is formed by the mbustion of the carbon of the fuel in the oxygen of the air entering at bottom of the grate; and this carbonic acid, in passing over the layer heated carbon in the upper part of the fire, is partly converted into bonic oxide, which inflames when it meets with the oxygen in the air ove the surface of the fuel, and burns with its characteristic blue flame, producing carbonic acid.

The carbonic oxide occupies twice the volume of the carbonic acid from ich it was produced.

This conversion of carbonic acid into carbonic oxide is of great import-ce on account of its extensive application in metallurgic operations. It often desirable, for instance, that a flame should be made to play over surface of an ore placed on the bed or hearth of a reverberatory fur-ce (fig. 76). This object is easily attained when the coal affords a large

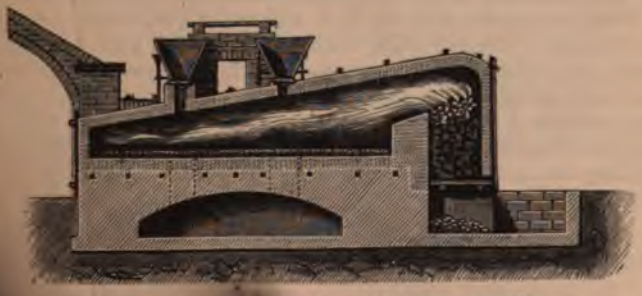


Fig. 76.—Rever[illegible]ory furnace for copper smelting.

[illegible] inflammable gas[illegible] anthracite coal, which burns with [illegible]me, and is frequ[illegible]oyed in such furnaces, it is neces-[illegible]*igh column of* [illegible] the grate, so that the carbonic

acid formed beneath may be converted into carbonic oxide in passing over the heated coal above, and when this gas reaches the hearth of the furnace, into which air is admitted, it burns with a flame which spreads over the surface of the ore.

The attraction of carbonic oxide for oxygen is turned to account in removing that element from combination with iron in its ores, as will be seen hereafter.

Carbonic oxide is a gas of so poisonous a character that, according to Leblanc, one volume of it diffused through 100 volumes of air totally unfits it to sustain life; and it appears that the lamentable accidents which too frequently occur from burning charcoal or coke in braziers and chafing-dishes in close rooms, result from the poisonous effects of the small quantity of carbonic oxide which is produced and escapes combustion, since the amount of carbonic acid thus diffused through the air is not sufficient in many cases to account for the fatal result.

63. The knowledge of this poisonous character of carbonic oxide gave rise, a few years since, to considerable apprehension when it was proposed to employ this gas in Paris for purposes of illumination. The character of the flame of carbonic oxide would appear to afford little promise of its utility as an illuminating agent; but that it is possible so to employ it is easily demonstrated, by kindling a jet of the gas which has been passed through a wide tube containing a little cotton moistened with rectified coal naphtha (benzole), when it will be found to burn with a very luminous flame. The carbonic oxide destined to be employed for illuminating purposes was prepared by passing steam over red-hot coke or charcoal, when a highly-inflammable gas was obtained, containing carbonic acid, carbonic oxide, and hydrogen—

$$4HO + C_3 = CO_2 + 2CO + H_4$$

Since neither hydrogen nor carbonic oxide burns with a luminous flame, this gas was next passed into a vessel containing red-hot coke, over which melted resin was allowed to trickle. The action of heat upon the resin gave rise to the production of vapours similar to that of the benzole employed in the above experiment, and which, in like manner, conferred considerable illuminating power upon the gas.

The decomposition of steam by red-hot carbon is also taken advantage of in order to procure a flame from anthracite coal when employed for heating boilers. The coal being burnt on *fish-bellied* bars, beneath which a quantity of water is placed, the radiated heat converts the water into steam, which is carried by the draught into the fire, where it furnishes carbonic oxide and hydrogen, both capable of burning with flame under the bottom of the boiler. The temperature of the bars is also thus reduced, so that they are not so much injured by the intense heat of the glowing fuel.

64. Carbonic oxide, unlike carbonic acid, is a permanent gas, and nearly insoluble in water. It is even lighter than air, its specific gravity being 0·967. In its chemical relations it is an indifferent oxide, that is, it has neither acid nor basic properties.

65. A very instructive process for obtaining carbonic oxide, consists in heating crystallised oxalic acid with three times its weight of oil of vitriol. If the gas be collected *over water* (fig. 77), and one of the jars be shaken with a little lime-

r, the milkiness imparted to the latter will indicate abundance of car-
acid; whilst, on removing
lass plate, and applying a
, the carbonic oxide will
with its characteristic blue
e. The gas thus obtained
mixture of equal volumes
rbonic oxide and carbonic
gases. Crystallised oxalic
is represented by the for-
$C_2HO_4 . 2Aq.$, and if the
r of crystallisation be left
f consideration, its decom-
ion may be represented by
equation—

Fig. 77.

$$C_2HO_4 = HO + CO + CO_2,$$

hange being determined by
ttraction of the oil of vitriol
ater. To obtain pure carbonic oxide, the mixture of gases must be passed
ugh a bottle containing solution of potash, to absorb the carbonic acid (fig. 78).
t pure carbonic oxide is much more easily obtained by the action of four parts
l of vitriol upon one part of crystallised ferrocyanide of potassium (yellow prus-

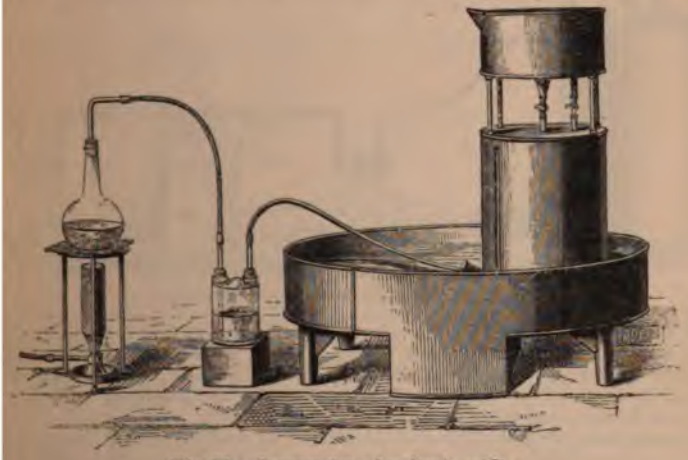


Fig. 78.—Preparation of carbonic oxide.

ot potash) at a moderate heat, the lamp being removed as soon as the effer-
nce begins to take place. Since the gas contains, especially at the commence-
, small incidental quantities of sulphurous and carbonic acids, it must be passed
gh solution of potash if it be required perfectly pure. The chemical change
h occurs in this process is expressed thus:—

$$\underset{\text{Ferrocyanide of potassium.}}{K_2C_6N_3Fe} + 6HO + 6(HO . SO_3) = 6CO + \underset{\text{Sulphate of potash.}}{2(KO . SO_3)}$$

$$+ \underset{\text{Sulphate of ammonia.}}{3(NH_3 . HO . SO_3)} + \underset{\text{Sulphate of iron.}}{FeO . SO_3}$$

. To demonstrate the production of carbonic acid during the combustion of
nic oxide, a jar of the gas is closed with a glass plate, and after placing it upon
able, the plate is slipped aside and a little lime-water quickly poured into the
On shaking, no milkiness indicative of carbonic acid should be perceived.
plate is then removed, and the gas kindled. On replacing the plate and
ng the jar, an abundant precipitation of carbonate of lime will take place.

When carbonic oxide is passed through a red-hot porcelain tube, a portion of it is decomposed into carbonic acid and carbon; and when the experiment is conducted without special arrangements, the carbonic oxide is reproduced as the temperature of the gas falls. But by passing through the centre of the porcelain tube a brass tube, through which cold water is kept running, the decomposition has been demonstrated by the deposition of carbon upon the cooled tube, and by collecting the carbonic acid formed.

Carbonic acid is also decomposed by intense heat into carbonic oxide and oxygen; but if these gases be allowed to cool down slowly in contact, they recombine. The gas drawn from the hottest region of a blast-furnace (*see* IRON), and rapidly cooled, so as to prevent recombination, was found to contain both carbonic oxide and oxygen.

By passing a pellet of phosphorus up into carbonic acid, over mercury, in a eudiometer, and passing electric sparks for some days, the gas has been entirely decomposed, an equal volume of carbonic oxide being left.

The reducing action of carbonic oxide upon metallic oxides, at high temperatures, may be illustrated by passing the pure gas from a bag or gas-holder (A, fig. 79), first through a bottle of lime-water (B) to prove the absence of carbonic acid, then over

Fig. 79.—Reduction of oxide of copper by carbonic oxide.

oxide of copper, contained in the tube C, and afterwards again through lime-water in D. When enough gas has been passed to expel the air, heat may be applied to the tube by the gauze-burner E, when the formation of carbonic acid will be immediately shown by the second portion of lime-water, and the black oxide of copper will be reduced to red metallic copper.

If precipitated peroxide of iron be substituted for oxide of copper, iron in the state of black powder will be left, and if allowed to cool in the stream of gas, will take fire when it is shaken out into the air, becoming reconverted into the peroxide (*iron pyrophorus*).

67. *Composition by volume of carbonic oxide and carbonic acid.*—When carbon burns in oxygen, the volume of the carbonic acid produced is exactly equal to that of the oxygen, so that one volume of oxygen furnishes one volume of carbonic acid gas.

If from the weight of one volume (*specific gravity*) of carbonic acid (1·529) there be deducted the weight (1·105) of one volume of oxygen, the remainder (·424) will represent the weight of carbon contained in one volume of carbonic acid; and if it be *assumed* that this carbon, were it possible to convert it into vapour, would occupy a volume equal to that of the oxygen (one volume), the number ·424 would represent the specific gravity of the *hypothetical* vapour of carbon, and one volume of carbonic d would be regarded as containing one volume of carbon vapour, com- *d with one* volume of oxygen.

When one volume of carbonic acid (containing one volume of oxygen) is passed over heated carbon, it yields two volumes of carbonic oxide; hence two volumes of this gas contain one volume of oxygen.

The weight of one volume (*specific gravity*) of carbonic oxide is 0·967, and the weight of two volumes, therefore, .	1·934
Deduct from this the weight of one volume of oxygen,	1·105
And the remainder, .	·829

represents the weight of carbon contained in two volumes of carbonic oxide. It was calculated above that ·424 expressed the weight of one volume of carbon vapour,—hence, allowing for errors in determining the specific gravities of the gases, ·829 may be taken to represent two volumes of carbon vapour, and carbonic oxide to contain, in two volumes, one volume of oxygen, combined with two volumes of the imaginary vapour of carbon.

This calculation is much simplified if hydrogen be made the unit of specific gravity, instead of atmospheric air:—

Specific gravity (to H) of CO_2, i.e., weight of one volume, .		22
Specific gravity (to H), or weight of one volume, of O, . .		16
Weight of carbon in one volume of CO_2, or assumed specific gravity (to H) of carbon vapour, ...		6
Specific gravity (to H), or weight of one volume, of CO,	14	
Weight of two volumes of CO, ...	28	
,, one volume of O, ...	16	
Weight of carbon in two volumes of CO, or assumed weight of two volumes of carbon vapour, . .		12

68. *Combining weight of carbonic acid.*—It will be remembered that in the decomposition of water by potassium (p. 23), 39 grs. of that metal displaced 1 gr. of hydrogen, combining with the 8 grs. of oxygen to form 47 grs. of potash (KO), whence 39 was termed the equivalent (to one of hydrogen) or combining weight of potassium, and 47 would represent the combining weight of potash. These 47 grs. of potash are found by experiment to combine with 22 grs. of carbonic acid, so that the number 22 may be taken for the combining weight of that acid.* Since it has been ascertained that in 22 parts of carbonic acid there are 6 parts of carbon, united with 16 of oxygen, and that, in carbonic oxide, the 6 parts of carbon are united with 8 parts of oxygen, the number 6 may be taken to represent the combining weight of carbon, or the weight equivalent to one of hydrogen.

If 8 parts by weight of oxygen be represented as occupying one volume (*see* p. 36), then the 11 parts of carbonic acid furnished by it would also occupy one volume, and one equivalent (22 parts) of carbonic acid would occupy two volumes, and would contain two volumes of imaginary carbon vapour, and two volumes of oxygen.

* It is true that 47 grs. of potash may also combine with 44 grs. of carbonic acid (simultaneously, however, with 9 grs. of water), but the compound (bicarbonate of potash) thus formed so easily loses one-half of its carbonic acid, that it is more natural to regard it as *containing two combining weights of the acid.*

The following table would then represent the equivalents and composition of carbonic oxide and carbonic acid :—

	Formula.	Equivalent Weight.	By Weight.		Equivalent Volume.	By Volume.	
			C	O		C	O
Carbonic oxide,	CO	14	6	8	2	2	1
Carbonic acid,	CO_2	22	6	16	2	2	2

69. The *atomic weight* (*see* p. 36) of carbon is generally assumed to be 12, though, in consequence of the impossibility of determining the weight of one volume of carbon vapour by experiment, the chemist is compelled to surrender himself in this matter to the guidance of analogy and purely theoretical considerations.

The *molecular formulæ* of carbonic oxide and carbonic acid would then become—

	Molecular Formula.	Molecular Weight.	By Weight.		Molecular Volume.	By Volume.	
			C	O		C	O
Carbonic oxide,	CO	28	12	16	2	1	1
Carbonic acid,	CO_2	44	12	32	2	1	2

Compounds of Carbon and Hydrogen.

70. No two elements are capable of occurring in so many different forms of combination as carbon and hydrogen. The *hydrocarbons*, as their compounds are generally designated, include most of the inflammable gases which are commonly met with, and a great number of the essential oils, naphthas, and other useful substances. There is reason to believe that all these bodies, even such as are found in the mineral kingdom, have been originally derived from vegetable sources, and their history belongs, therefore, to the department of organic chemistry. The three simplest examples of such compounds will, however, be brought forward in this place, to afford a general insight into the mutual relations of these two important elements. Their names and composition are—

	Equivalent Formulæ.*	Parts by Weight.	
		C	H
Acetylene, . .	C_4H_2	24	2
Marsh-gas, . .	C_2H_4	12	4
Olefiant gas, .	C_4H_4	24	4

* The reasons why these formulæ should not be written respectively C_2H, CH_2, and

*cetylene.**—When very intensely heated, carbon is capable of ng with hydrogen to form acetylene. The requisite heat is pro- means of a powerful galvanic battery, to the terminal wires of vo pieces of dense carbon are attached, and the voltaic discharge is to take place between them in an atmosphere of hydrogen. The ent possesses little practical importance, because but little acety- formed in proportion to the force employed, but its theoretical is very great, since it is the first step in the production of organic es by the direct synthesis of mineral elements; acetylene (C_2H_2) nvertible into olefiant gas (C_2H_4), this last into alcohol ($C_4H_6O_2$), hol into a very large number of organic products.

lene is constantly found among the products of the incomplete ion and destructive distilla- substances rich in carbon, is always present in small in coal-gas, and may be pro- abundance by passing the of ether through a red-hot The character by which acety- nost easily recognised is that icing a fine red precipitate in ioniacal solution of cuprous (subchloride of copper).

ost convenient process for pre- quantity of this precipitate, is hich the acetylene is produced perfect combustion taking place t of atmospheric air is allowed n coal-gas.

yter (A, fig. 80) is connected at w end with the pipe supplying The wider opening is closed by a h two holes, one of which receives of brass tube (B) about three- of an inch wide and seven inches in the other is inserted a glass which conducts the gas to the f a *separating funnel* (D). The ning of the brass tube B is closed

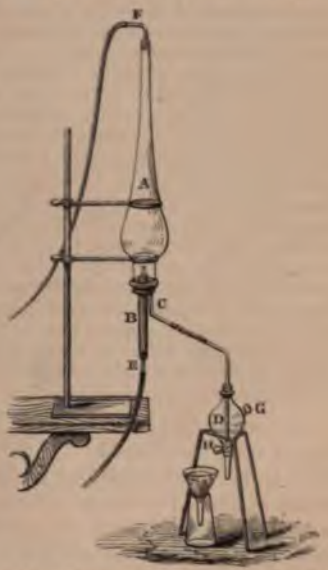


Fig. 80.—Preparation of cuprous acetylide.

rk, through which passes the glass tube E connected with a gas-holder or bag g atmospheric air. To commence the operation, the gas is turned on the tube F, and when all air is supposed to be expelled, the tube E is with- gether with its cork, and a light is applied to the lower opening of the e, the supply of coal-gas being so regulated that it shall burn with a small the end of the tube. A feeble current of air is then allowed to issue from E, which is passed up through the flame into the adapter, where the jet tinues to burn in the coal-gas,† and may be kept burning for hours with

h would, of course, agree equally well with the results of analysis, will appear

lecular formulæ would be—

Acetylene,	$\Theta_2H_2 = 2$ vols.
Marsh-gas,	$\Theta H_4 = 2$ vols.
Olefiant gas,	$\Theta_2H_4 = 2$ vols.

where $\Theta = 12$.

known as *klumene*, having been obtained in 1836 by the action of water upon a l containing carbon and potassium, produced during the preparation of that The name acetylene is derived from the hypothetical radical acetyle (C_4H_2), to tylene bears the same relation as ethylene (C_4H_4) does to ethyle (C_4H_5).

dvisable to attach a piece of thin platinum wire to the mouth of the glass tube, *he flame of the air more visible.*

a little attention to the proportions in which the gas and air are supplied. A solution of subchloride of copper in ammonia is poured into the separating funnel through the lateral opening G, so that the imperfectly burnt gas may pass through it, when the cuprous acetylide is precipitated in abundance. When a sufficient quantity has been formed, or the copper solution is exhausted, the liquid is run out through the stop-cock (H) on to a filter, and replaced by a fresh portion. The precipitate may be rinsed into a flask provided with a funnel tube and delivery tube, allowed to subside, the water decanted from it, and some strong hydrochloric acid poured in through the funnel. On heating, the acetylene is evolved, and may be collected, either over water, or more economically in a small gas-bag. To obtain a pint of the gas, as much of the moist copper precipitate is required as will measure about six ounces after settling down. Such a quantity may be prepared in about six hours.

A solution of cuprous chloride suitable for this experiment is conveniently prepared in the following manner: 500 grains of black oxide of copper are dissolved in seven measured ounces of common hydrochloric acid, in a flask, and boiled for about twenty minutes with 400 grains of copper in filings or fine turnings. The brown solution of cuprous chloride in hydrochloric acid thus obtained is poured into about three pints of water contained in a bottle; the white precipitate (cuprous chloride) is allowed to subside, the water drawn off with a siphon, and the precipitate rinsed into a twenty-ounce bottle, which is then quite filled with water and closed with a stopper. When the precipitate has again subsided, the water is drawn off, and four ounces of powdered chloride of ammonium are introduced, the bottle being again filled up with water, closed and shaken. The cuprous chloride is entirely dissolved by the chloride of ammonium, but would be reprecipitated if more water were added. When required for the precipitation of acetylene, the solution may be mixed with about one-tenth of its bulk of strong ammonia (·880), which may be poured into the separating funnel (D) before the copper solution is introduced. Four measured ounces of the solution are sufficient for one charge, and yield, in three hours, about three measured ounces of the moist precipitate. The blue solution of ammoniacal cupric chloride filtered from the red precipitate may be rendered serviceable again by being shaken, in a stoppered bottle, with precipitated copper, prepared by reducing a solution of sulphate of copper, acidulated with hydrochloric acid, with a plate of zinc.

The red precipitate is said to consist chiefly of the oxide of a compound formed from acetylene by the substitution of Cu_2 for H. This compound, C_4Cu_2H, has been named by Berthelot *cupros-acetyle*, and may be regarded as the radical of a series of compounds. If but little free ammonia be present in the solution of cuprous chloride, the precipitate will contain the chloride of cuprous-acetyle, $(C_4Cu_2H)\,Cl$, as well as the oxide.

If the acetylene copper precipitate be collected on a filter, washed, and dried either by mere exposure to the air, or over oil of vitriol, it will be found to explode with some violence when gently heated, and it is said that the accidental formation of this compound in copper or brass pipes, through which coal-gas passes, has occasionally given rise to explosions.

When acetylene is passed through solution of nitrate of silver, a white curdy precipitate is formed, resembling chloride of silver in appearance, but insoluble in ammonia (which turns it yellow) as well as in nitric acid. It may be obtained by allowing the imperfectly burnt gas from the apparatus in fig. 80 to pass through nitrate of silver.

When this precipitate is washed and allowed to dry, it is violently explosive if heated, though it may be hammered without exploding. A minute fragment of it placed on a glass plate, and touched with a red-hot wire, detonates loudly and shatters the glass like fulminate of silver. The explosive silver compound is said to contain the *oxide of argent-acetyle* $(C_4Ag_2H)O$, the chloride corresponding to it, $(C_4Ag_2H)\,Cl$, being precipitated when acetylene is passed through a solution of chloride of silver in ammonia. In a solution of hyposulphite of gold and sodium, acetylene gives a yellowish very explosive precipitate.

When potassium or sodium is heated in excess of acetylene, it is said that one *of the* hydrogen is displaced by the metal, forming acetylide of potassium *HK) or of* sodium (C_4HNa), a portion of the acetylene being converted into dek-

) by combination with the displaced hydrogen. When heated to dull red- completely decomposes acetylene, C_4Na_2 being obtained. Both these ounds are violently decomposed by water, acetylene being reproduced. s formation of acetylene during the imperfect combustion of ether is hown by introducing a few drops of ether into a test-tube, adding a iacal solution of cuprous chloride, kindling the ether-vapour at the tube, and inclining the latter so as to expose a large surface of the n, when a large quantity of the red cuprous acetylide is produced. If er be substituted for the copper solution, the white precipitate of oxide yle is formed abundantly.
has been found accompanying the vapour of hydrocyanate of ammonia he action of ammonia on red-hot charcoal.

e is a colourless gas having a peculiar odour, recalling that of m, which is always perceived where coal-gas is undergoing ombustion. It burns with a very bright smoky flame. Its kable property is that of inflaming spontaneously when brought with chlorine. If a jet of the gas be allowed to pass into a lorine, it will take fire and burn with a red flame depositing n. When chlorine is decanted up into a cylinder containing tanding over water, a violent explosion immediately takes led with a vivid flash, and separation of a large amount of $H_2 + Cl_2 = C_4 + 2HCl$.
etylene is passed into water, it is absorbed in sufficient quan- rt a strong smell to the water, and to yield a decided precipi- mmoniacal cuprous chloride and with nitrate of silver.
n of heat upon acetylene is very remarkable and instructive, lts in the formation of a complex body from one which is less composition. When heated in a glass tube for half an hour at which the glass began to soften, it was found to be re- e-fifth of its original volume, the greater portion of it having ted into a liquid hydrocarbon *styrole*, $C_{16}H_8$, hitherto obtained getable gum-resin known as storax. The remaining gas was ogen (a little carbon having separated) with a little olefiant heated in contact with coke or iron, the bulk of the acety- nposed into its elements.
ding the acetylene copper precipitate in solution of ammonia, with a little granulated zinc, Berthelot has induced the acety- bine with the (*nas-* en to form olefiant

ant gas.—This gas arger quantity than mong the products of heat upon coal, bstances rich in car- is one of the most constituents of the gases obtained from ls.
gas may readily be the action of strong cid (oil of vitriol, pon alcohol (spirit of wine $C_4H_6O_2$).

Fig. 81.—Preparation of olefiant gas.

es of oil of vitriol are introduced into a flask (fig. 81), and one measure

of alcohol is gradually poured in, the flask being agitated after each addition acid; much heat is evolved, and there would be danger in mixing large v suddenly.* On applying a moderate heat, the will darken in colour, effervescence will take and the gas may be collected in jars fille water. When the mixture has become thic the evolution of the gas is slow, the end of t must be removed from the water and the la tinguished.

Fig. 82.

The gas will be found to have a very p odour, in which that of ether and of sulphuro are perceptible. One of the jars may be clos a glass plate, and placed upon the table w mouth upwards; on the approach of a flame will take fire, burning with a bright white flam acteristic of olefiant gas, and seen to best adv when, after kindling the gas, a stream of w poured down into the jar in order to displace (fig. 82.)

Another jar of the gas may be well was transferring it repeatedly from one jar to a under water, a little solution of potash may b poured into it, and the jar violently shal mouth being covered with a glass plate; the will remove all the sulphurous acid, and the g now exhibit the peculiar faint odour which to olefiant gas.

The purified gas may be transferred, under water, to another jar, kindl allowed to burn out; if a little lime-water be then shaken in the jar, its turbid indicate the presence of carbonic acid, which is produced, together with wate olefiant gas burns in air: $C_4H_4 + O_{12} = 4CO_2 + 4HO$.

On comparing the composition of olefiant gas (C_4H_4) with t alcohol ($C_4H_6O_2$), it is evident th former may be supposed to be pr from the latter by the abstraction equivalents of water (H_2O_2) which moved by the sulphuric acid, thougl secondary changes take place, re in the separation of carbonaceous and the production of sulphurou A more complete explanation of the of sulphuric acid upon alcohol must served for the chemical history compound.

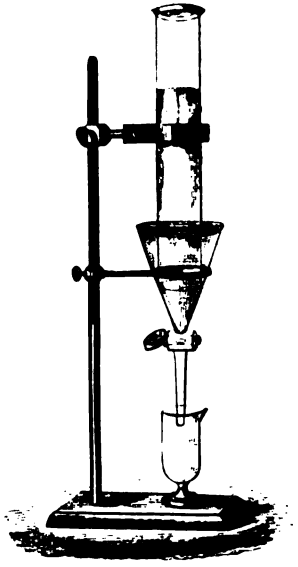


Fig. 83.

Olefiant gas derives its name fr property of uniting with chlorine a mine to form oily liquids, a circun which is applied for the determina the proportion of this gas present i gas, upon which great part of the illu ing value of coal-gas depends. Th pound with chlorine ($C_4H_4Cl_2$) is as *Dutch liquid*, having been discov Dutch chemists, and is remarkable resemblance to chloroform in odour.

To exhibit the formation of Dutch l *quart cylinder* (fig 83) is half filled with olefiant gas, and half with chlorin

* *If methylated spirit* be employed, the mixture will have a dark red-brown co

ssed up into it, from a bottle of the gas, under water. The cylinder is with a glass plate, and supported with its mouth downwards under water *ing funnel* furnished with a glass stop-cock. The volume of the mixed to diminish immediately, drops of oil being formed upon the side of and the surface of the water. As the drops increase, they fall to the e funnel. Water must be poured into the funnel to replace that which e cylinder, and when the whole of the gas has disappeared, the oil may t of the funnel through the stop-cock into a test-glass, in which it is a little potash to absorb any excess of chlorine. The fragrant odour of the will then be perceived, especially on pouring it out into a shallow dish. structive experiment consists in filling a three-pint cylinder one-third nt gas, then rapidly filling it up, under water, with two pints of chlorine, outh with a glass plate, shaking it to mix the gases, slipping the plate plying a light, when the mixture burns with a red flame which passes own the cylinder, and is due to the combination of the hydrogen with , the whole of the carbon being separated in te—

$$C_4H_4 + Cl_4 = 4HCl + C_4$$

lefiant gas is subjected to the action of eratures, as by passing through heated portion is decomposed into marsh-gas h separation of carbon, whilst another lds acetylene (C_4H_2) and hydrogen; these ions will be found to be of great impor- e manufacture of coal-gas.

Fig. 84.

a of heat upon olefiant gas is most conveniently posing it to the spark from an induction coil. confined in a tube (A, fig. 84) which is placed cal jar (B) containing mercury. Through the ses a copper wire (C) thrust through a glass insulate it from the mercury; this wire is con- one of the wires (E) from the induction coil, her (F) is allowed to dip into the mercury contained in the cylinder the coil in action (with two or three cells of Grove's battery), the spark ween the extremity sulated copper wire ace of the mercury , decomposing the in its passage, and paration of carbon, times forms a con- mmunication, and rrent to pass with- This may be ob- ersing the current, shaking the tube. nt gas will expand to its former volume, tube will gradually mercury, but the ce may always be for the passage of

Fig. 85.—Preparation of cuprous acety olefiant gas.

the production of nother arrangement nd convenient (fig. be with four necks ; through two of are passed, air-tight ted corks, the cop- *nected with the in- A third neck re-*

ceives a tube, conveying olefiant gas from a gas-holder, whilst from th proceeds a tube dipping to the bottom of a small cylinder. When the the air has been displaced by olefiant gas, a solution of sub-chloride of c ammonia is poured into the cylinder, and the gas allowed to bubble th when the absence of acetylene will be shown by there being no red c formed. As soon, however, as the spark is passed the red precipitate wil and, in a very few minutes, a large quantity will be deposited. Coal-gas employed instead of olefiant gas, but of course less of the copper-compoun obtained.

73. *Marsh-gas*, or *light carburetted hydrogen*.—Unlike acetyl olefiant gas, this hydrocarbon is found in nature, being produced w vegetable matter is undergoing decomposition in the presence of m The bubbles rising from stagnant pools, when collected and exami found to contain marsh-gas mixed with carbonic acid, and there i to believe that these two gases represent the principal forms in wh hydrogen and oxygen respectively were separated from wood dur process of its conversion into coal. This would account for the c presence of this gas in the coal-formations, where it is usually term *damp*. It is occasionally found pent up under pressure between th of coal, and the pores of the latter are sometimes so full of it that be seen rising in bubbles when the freshly hewn coal is throv water. Perhaps a similar origin is to be ascribed to the liquid carbons chemically similar to marsh-gas, which are found so abu in Pennsylvania and Canada, and are known by the general r *petroleum*.

Marsh-gas is obtained artificially by the following process :—

500 grains of dried acetate of soda are finely powdered, and mixed, in a with 200 grains of solid hydrate of potash, and 300 grains of powdered q (or with 500 grains of the mixture of hydrate of lime and hydrate of soda, sold as *soda-lime*). The mixture is heated in a Florence flask (or better, tube, for the alkali corrodes the glass), and the gas collected over water (fig.

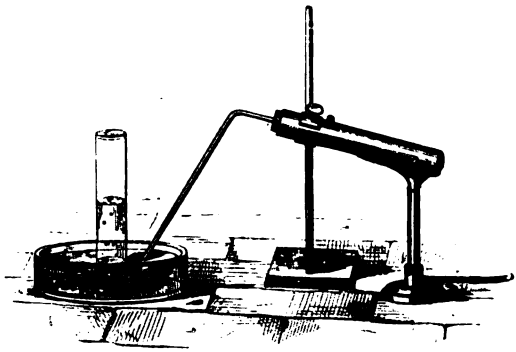


Fig. 86.—Preparation of marsh-gas.

The decomposition will be evident from the following equation :—

$$\underset{\text{Acetate of soda.}}{NaO.C_4H_3O_3} + \underset{\text{Hydrate of potash.}}{KO.HO} = \underset{\text{Carb. of soda.}}{NaO.CO_2} + \underset{\text{Carb. of potash.}}{KO.CO_2} + C$$

The marsh-gas will be easily recognised by its burning with illuminating flame, far inferior in brilliancy to those of olefiant g acetylene, but unattended with smoke.

The properties of this gas deserve a careful study, on account tent *fatal* explosions to which it gives rise in coal-mines, wh

often found accumulated under pressure, and discharging itself with considerable force from the fissures or *blowers* made in hewing the coal. Marsh-gas has no characteristic smell like coal-gas, and the miner thence receives no timely warning of its presence; it is much lighter than air (sp. gr. 0·5596), and therefore very readily diffuses* itself (page 29) through the air of the mine, with which it forms an explosive mixture as soon as it amounts to one-eighteenth of the volume of the air. The gas issuing from the blower would burn quietly on the application of a light, since the marsh-gas is not explosive unless mixed with the air, when a large volume of the gas is burnt in an instant, causing a sudden evolution of a great deal of heat, and a consequent sudden expansion or explosion exerting great mechanical force. The most violent explosion takes place when one volume of marsh-gas is mixed with two volumes of oxygen, since this quantity is exactly sufficient to effect the complete combustion of the carbon and hydrogen of the gas, and therefore to evolve the greatest amount of heat: $C_2H_4 + O_2 = 2CO_2 + 4HO$. The calculated pressure exerted by the exploding mixture of marsh-gas and oxygen amounts to 37 atmospheres, or 555 lbs. upon the square inch. Since air contains one-fifth of its volume of oxygen, it would be necessary to employ ten volumes of air to one volume of marsh-gas in order to obtain perfect combustion, but the explosion will be much less violent on account of the presence of the eight volumes of inert nitrogen, the calculated pressure exerted by the explosion being only 14 atmospheres, or 210 lbs. on the square inch. Of course, if more air is employed, the explosion will be proportionally weaker, until, when there are more than eighteen volumes of air to each volume of marsh-gas, the mixture will be no longer explosive, but will burn with a pale flame around a taper immersed in it. The carbonic acid resulting from the explosion is called by miners the *after-damp*, and its effects are generally fatal to those who may have escaped death from the explosion itself.

Fortunately, marsh-gas requires a much higher temperature to inflame it than most other inflammable gases; thus a solid body at an ordinary red heat does not kindle the gas, contact with flame, or with a body heated to whiteness, being required to ignite it.

If two strong gas-cylinders be filled, respectively, with mixtures of 2 vols. hydrogen with 1 vol. oxygen, and of 1 vol. marsh-gas and 2 vols. oxygen, it will be found, on holding them with their mouths downwards, and inserting a red-hot iron bar, that the marsh-gas mixture will not explode, but if the bar be transferred at once to the hydrogen mixture, explosion will take place. A lighted taper may then be used to explode the marsh-gas and hydrogen.

Coal-gas, although answering very well for many illustrations of the properties of marsh-gas, cannot be used in this experiment, since some of its constituents inflame at a far lower temperature.

In consequence of the high temperature required to inflame the mixture of marsh-gas and air, it is neces[illegible] mixture be allowed to remain for an appreciable time in conta[illegible]me before its particles are raised to the igniting point. [illegible]nciple that Stephenson's original safety lamp was consi[illegible]ning surrounded with a tall glass chimney, the rapid [illegible]h caused the explosive mixture to be hurried past the [illegible]e.

* *Ansell's fire-damp indicator* is [illegible] high rate of diffusion of marsh-gas is taken advantage of in [illegible] in the air of mines. The *experiment described at page 29 illus-*

To illustrate this, a copper funnel (fig. 87) holding about two quarts is employed, the neck of which has an opening of about ¼ inch in diameter, The funnel being placed mouth downwards in the pneumatic trough, the orifice is closed with the

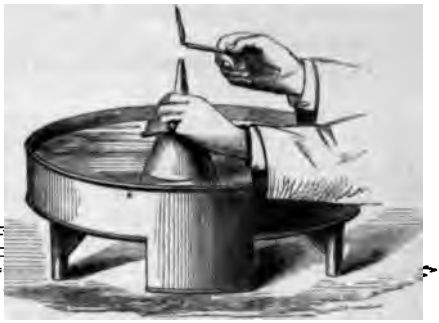


Fig. 87.

finger, and half a pint of coal-gas passed up into the funnel. The latter is now raised from the water, so that it may become entirely filled with air. By depressing the funnel to a considerable depth in the water, the aperture being still closed by the finger, the mixture will be confined under considerable pressure, and if a lighted taper be held to the aperture, and the finger removed, it will be found that the mixture sweeps past the flame without exploding, until the water has reached the same level in the funnel as in the trough, when the gas comes to rest and explodes with great violence.

Fig. 88.—Davy lamp.

Davy's safety lamp (fig. 88) is an application of the principle that ignited gas (*flame*) is extinguished by contact with a large surface of a good conductor of heat, such as copper or iron.

If a thin copper wire be coiled round into a helix, and carefully placed over the wick of a burning taper (fig. 89), the flame will be at once extinguished, its heat being so rapidly transmitted along the wire that the temperature falls below the point at which the combustible gases enter into combination with oxygen, and therefore the combustion ceases. If the coil be heated to redness in a spirit-lamp flame before placing it over the wick, it will not abstract the heat so readily, and will not extinguish the flame. If a copper tube were substituted for the coiled wire, the same result would be obtained, and by employing a number of tubes of very small diameter, so that the metallic surface may be very large in proportion to the volume of ignited gas, the most energetic combustion may be arrested, as in the case of *Hemming's safety jet*, which consists of a brass tube tightly stuffed with thin copper wires so as to leave very narrow passages, thus rendering it impossible for the oxyhydrogen flame at the jet to pass back and ignite the mixture in the reservoir.

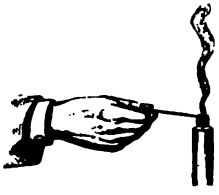


Fig. 89.

It is evident that the exposure of a large extent of cooling surface to the action of the flame, may be effected either by increasing the length or by diminishing the width of the metallic tubes, so that wire gauze, which may be regarded as a collection of very short tubes, will form an effectual barrier to flame, provided that it has a sufficient number of meshes to the inch.

If a piece of iron wire gauze, containing about 800 meshes to the square inch, be depressed upon a flame, it will extinguish that portion with which it is in contact, and the combustible gas which escapes through the gauze may be kindled by a lighted match held on the upper side. By holding the gauze two or three inches *above a gas jet*, the gas may be lighted above it without communicating the flame *o the burner itself*.

lazing spirit is poured upon a piece of wire gauze (fig. 90) the flame will on the gauze, and the extinguished spirit will pass through. A little turpentine may be added to the spirit s flame may be more visible at a dis-

Fig. 90.

afety lamp is an oil lamp, the flame is surrounded by a cage of iron ze, having 700 or 800 meshes in re inch, and made double at the top e heat of the flame chiefly plays. e is protected by stout iron wires to a ring for suspending the lamp. tube passes up through the oil , and in this there slides, with con- friction, a wire bent at the top, so that the wick may be trimmed taking off the cage.

lamp be suspended in a large jar, closed at the top with a perforated over (A, fig. 91), and having an aperture (B) below, through which coal- be admitted, the lamp will burn, of course, in ary way; but if the gas be allowed to pass o the jar, the flame will be seen to waver, to itself very considerably, and will be ultimately hed, when the wire cage will be seen to be h a mixture of coal-gas and air burning tran- thin the gauze, which prevents the flame from o ignite the explosive atmosphere surrounding ; that an explosive mixture really fills the jar eadily ascertained by introducing, through an (C) in the cover, the unprotected flame of a en an explosion will take place.

Fig. 91.

xperiment illustrates the action of the Davy mine which contains fire-damp, and makes it hat this lamp would afford complete protection ly used. It would obviously be unsafe to allow to remain in the explosive mixture when the illed with flame, for the gauze would either ufficiently heated to kindle the surrounding gas, or would be oxidised and o holes, which would allow the passage of the flame. Nor should the lamp ed to a very strong current, which might possibly be able to carry the flame the meshes.

great defect of the Davy lamp is that it does not afford more than ering light, so that even if the miners were prohibited from em- any candles, they would (and experience has proved that they do) the wire cage at all risks. The lamp has been modified so as par- remove this defect, by substituting glass or talc for some portions vire gauze. It is now usual, however, to employ the Davy lamp in order to test the state of the air in the different parts of the for this purpose the *firemen* descend before the commencement every morning, and examine with their safety lamps every portion ine, giving warning to the miners not to approach those parts in ny accumulation of fire-damp (or technically, "sulphur") is per- The miners then work with naked candles, and it appears to be usual to see a blue flame (or *corpse light*) playing around the , so that the miners may become accustomed to regard with little the very indication which shows that the quantity of fire-damp little below that required to form an explosive mixture. W *ked flames are used in the mine* there must always be great

in most seams of coal there are considerable accumulations of fire-damp; when a fissure is made, the gas escapes very rapidly from the *blower*, and the air in its vicinity may soon become converted into an explosive mixture. In mines where small quantities of fire-damp are known to be continually escaping from the coal, ventilation is depended upon in order to dilute the gas with so large a volume of air that it is no longer explosive, and finally to sweep it out of the mine; but it has occasionally happened that the ventilation has been interfered with by a door having been left open in one of the galleries, or by a passage having been obstructed through the accidental falling in of a portion of the coal, and an explosive mixture has then been formed.

Structure of Flame.

74. The consideration of the structure and properties of ordinary flames is necessarily connected with the history of olefiant gas and marsh-gas. Flame may be defined as gaseous matter, heated to the temperature at which it becomes visible, or emits light. Solid particles begin, for the most part, to emit light when heated to about 1000° F.; but gases, on account of their greater expansibility, must be raised to a far higher temperature, and hence the point of visibility is seldom attained, except by gases which are themselves combustible, and therefore capable of producing, by their own combination with atmospheric oxygen, the requisite degree of heat. The presence of a combustible gas (or vapour), therefore, is one of the conditions of the existence of flame; a diamond, or a piece of thoroughly carbonised charcoal, will burn in oxygen with a steady glow, but without flame, since the carbon is not capable of conversion into vapour, while sulphur burns with a voluminous flame, in consequence of the facility with which it assumes the vaporous condition. It will be observed, moreover, that in the case of a non-volatile combustible, the combination with oxygen is confined to the surface of contact, whilst in the flame of a gas or vapour, the combustion extends to a considerable depth, the oxygen intermingling with the gaseous fuel.

Flames may be conveniently spoken of as *simple* or *compound*, accordingly as they involve one or more phenomena of combustion; thus, for example, the flames of hydrogen and carbonic oxide are simple, whilst those of marsh-gas and olefiant gas are compound, since they involve both the conversion of hydrogen into water and of carbon into carbonic acid.

It is obvious that simple flames must be hollow in ordinary cases, such as that of a gas issuing from a tube into the air, the hollow being occupied by the combustible gas to which the oxygen does not penetrate.

All the flames which are ordinarily turned to useful account are compound flames, and involve several distinct phenomena. Before examining these more particularly, it will be advantageous to point out the conditions which regulate the luminosity of flames.

Just as gaseous matter is essential to the existence of flame, the presence of solid particles suspended in the flame is essential to its luminosity.

It has been seen that, when sulphur burns in oxygen, it emits a pale lurid light, whilst phosphorus, under similar circumstances, yields an intolerable blaze; this is easily explained, for the product of the combustion of sulphur, sulphurous acid, is gaseous at this temperature, but the lid phosphoric acid, formed from the phosphorus, is suspended in the *in a state of* very minute division, and becomes heated to so high

a degree as to emit a beautiful white light. That this is a true account of the matter is seen by introducing the phosphorus into a jar of chlorine gas, when it burns with a flame which is even paler than that of sulphur in oxygen, since the chloride of phosphorus which is formed is a vapour at the temperature of the combustion.

It is not necessary that the suspended solid matter should be a product of the combustion; any extraneous solid in a finely divided state will confer illuminating power upon a flame. Thus, the flame of hydrogen may be rendered highly luminous by burning a piece of phosphorus in its vicinity, so that the clouds of phosphoric acid may pass through the flame, or by blowing a little very fine charcoal powder into it, from the bottle represented in fig. 92.

Fig. 92.

The luminosity of all ordinary flames is due to the presence of highly heated carbon in a state of very minute division, and it remains to consider the changes by which this finely divided carbon is separated in the flame.

A candle, a lamp, and a gas-burner, exhibit contrivances for procuring light artifically in different degrees of complexity, the candle being the most complex of the three. When a new candle is lighted, the first portion of the wick is burnt away until the heat reaches that part which is saturated with the wax or tallow of which the candle is composed; this wax or tallow then undergoes destructive distillation, yielding a variety of products, among which olefiant gas is found in abundance. The flame furnished by the combustion of these products melts the fuel around the base of the wick, through which it then mounts by capillary attraction, to be decomposed in its turn, and to furnish fresh gases for the maintenance of the flame. In a lamp, the fuel being liquid at the commencement, the process of fusion is dispensed with; and in a gas-burner, where the fuel is supplied in a gaseous form, the process of destructive distillation has been already carried on at a distance. It will be seen, however, that the final result is similar in all three cases, the flame being maintained by such gases as acetylene, marsh-gas, and olefiant gas, arising from the destructive distillation of wax, tallow, oil, coal, &c.

Fig. 93.

On examining an ordinary flame, that of a candle, for instance, it is seen to consist of three concentric cones (fig. 93), the innermost, around the wick, appearing almost black, the next emitting a bright white light, and the outermost being so pale as to be scarcely visible in broad daylight.

The dark innermost cone consists merely of the gaseous combustible to which the air does not penetrate, and which is therefore not in a state of combustion.

The nature of this cone is easily shown by experiment: a strip of cardboard held across the flame near its base will not burn in the centre where it traverses the innermost cone; a piece of wire gauze depressed upon the flame near the wick (fig. 94) will allow the passage of *the combustible gas, which may be kindled above* it. The gas may be conv

Fig. 94.

of the flame by means of a glass tube inserted into the innermost cone, and kindled at the other extremity of the tube, which should be inclined dow (fig. 95).

A piece of phosphorus in a small spoon held in the interior of the flame of a

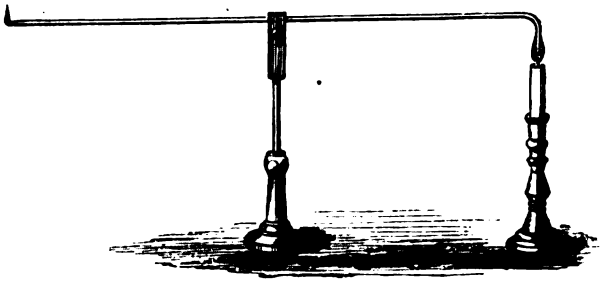


Fig. 95.

lamp, will melt and boil, but will not burn unless it be removed from the flar may then be extinguished by replacing it in the flame.

The combustible gas from the interior of a flame may be collected in (fig. 96) furnished with two tubes, one of which (A) is drawn out to a p insertion into the flame, whilst the other (B), which to the bottom of the flask, is bent over and prolong piece of vulcanised tubing, so that it may act as a The flask is filled up with water, the jet inserted i interior of a flame, and the siphon set running by e ing it with the mouth. As the water flows out thro siphon, the gas is drawn into the flask, and after re the tube from the flame, the gas may be expel blowing down the siphon tube, and may be burnt at When a candle is used for this experiment, some sol ducts of destructive distillation will be found conde the flask.

Fig. 96.

In the second or luminous cone, combustion is taking place, bu by no means perfect, being attended by the separation of a quan carbon, which confers luminosity upon this part of the flame. presence of free carbon is shown by depressing a piece of porcelai this cone, when a black film of soot is deposited. The liberation carbon is due to the decomposition of the olefiant gas and similar carbons by the heat, which separates the carbon from the hydroge this latter, undergoing combustion, evolves sufficient heat to rai separated carbon to a white heat, the supply of air which penetrat this portion of the flame being insufficient to effect the combustion whole of the carbon.

Some very simple experiments will illustrate the nature of the luminous po flame.

Over an ordinary candle flame (fig. 97) a tube may be adjusted so as t the finely-divided carbon from the luminous part of the flame into th hydrogen, which will thus be rendered as luminous as the candle flam colour of the carbon being apparent in its passage through the tube.

A bottle furnished with two straight tubes (fig. 98) is connected with a of hydrogen. One of the tubes is provided with a small piece of w taining a tuft of cotton wool. On kindling the gas at the orifice of difference will be seen in the flames until a drop of benzole ($C_{12}H_6$) i the cotton, when its vapour, mingling with the hydrogen, will furnish a to render the flame brilliantly luminous.

The pale outermost cone, or *mantle*, of the flame, in which on *is finally* consumed, may be termed the cone of perfect

much thinner than the luminous cone, the supply of air to this external shell of flame being unlimited, and the combustion therefore speedily effected.

Fig. 97.

Fig. 98.

The mantle of the flame may be rendered more visible by burning a little sodium near the flame, when the mantle is tinged strongly yellow.

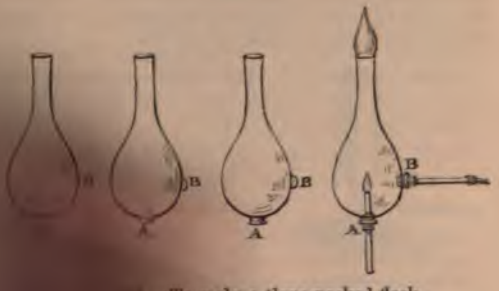
By means of a siphon about one-third of an inch in diameter (fig. 99), the nature of the different portions of an ordinary candle flame may be very elegantly shown. If the orifice of the siphon be brought just over the extremity of the wick, the combustible gases and vapours will pass through it, and may be collected in a small flask, where they can be kindled by a taper. On raising the orifice into the luminous portion of the flame, voluminous clouds of black smoke will pour over into the flask, and if the siphon be now raised a little above the point of the flame, carbonic acid can be collected in the flask, and may be recognised by shaking with lime-water.

Fig. 99.

The reciprocal nature of the relation between the combustible gas and the air which supports its combustion may be illustrated in a striking manner by burning a jet of air in an atmosphere of coal-gas.

A quart glass globe with three necks is connected at A (fig. 100) with the gas-pipe by a vulcanised tube. The second neck (B), at the upper part of the globe, is connected by a short piece of vulcanised tube with a piece of glass tube about ½ inch wide, from which the gas may be burnt. Into the third and lowermost neck is inserted, by means of a cork, a thin brass tube, C (an old cork-borer), about ¼ inch in diameter. When the gas is turned on, it may be lighted at the upper neck; and if a lighted match be then quickly thrust up the tube C, the air which enters it will take fire and burn inside the globe.

Fig. 100.—Air burning in coal-gas.



—To make a three-necked flask.

A very inexpensive apparatus may be constructed from a common Florence oil-flask. By applying heat at A (fig. 101), so as to heat to

whiteness a spot as large as a threepenny-piece, and quickly blowing in of the flask, the heated portion of the glass may be made to bulge out. protuberance is then to be formed at B. A sharp-pointed flame is direc and the glass burst by blowing into the flask whilst it is still exposed t By fusing the edges of the hole thus produced, and turning them outwar end of a file, a short neck may be formed capable of receiving a cork. is cool it is closed with a cork, and a second similar neck is produced at

From this review of the structure of flame, it is evident that to secure a flame which shall be useful for illumination, attentio paid to the supply of oxygen (or air), and to the composition o employed. The use of the chimney of an Argand burner (fig. 1(an instance of the necessity for attent proper supply of air. Without the chi flame is red at the edges and smok supply of air is not sufficient to con whole of the carbon which is separ the temperature is not competent to a bright white heat, defects which are as soon as the chimney is placed ov the rapidly-ascending heated column of in a liberal supply beneath the burne cated by the arrows.

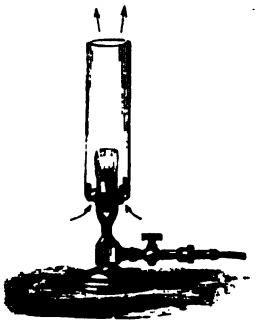


Fig. 102.—Argand burner.

By using two chimneys, and causir to pass down between them, so as to to about 500° F. before reaching the equal amount of light may be obtain much smaller supply of gas.

The smokeless gas-burners employed in laboratories and kitchei the result of mixing the gas with a considerable proportion of burning it, the luminous part of the flame tirely disappearing, with great augmentati temperature of the flame, since the carbor simultaneously with the hydrogen.

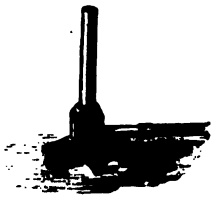


Fig. 103.—Bunsen's burner.

The most efficient burner of this kind (*Bun* fig. 103) is that in which the gas is conveyed i tube, at the base of which there are four large h admission of air. When a good supply of ga on, a quantity of air is drawn in through the l tures, and the mixture of air and gas may be the orifice of the wide tube, its rapid motion prev flame from passing down within the tube. This tube is sometimes surm a rosette burner to distribute the flame. By closing the air-holes with t a luminous flame is at once produced.

Fig. 104.—Gauze burner.

The principle of this burner has been applied the illuminating value of gas, by measuring th of air which must be supplied to a flame consumi quantity of gas, in order to destroy the lumir illuminating value being proportional to the q air which is necessary for this purpose.

The *gauze burner* (fig. 104) consists of an ope surmounted by wire gauze. When this is place gas-burner, a supply of air is drawn in at the l the ascending stream of gas, and the mixture b the gauze with a very hot smokeless flame, th meshes preventing the flame from passing down below.

The *luminosity* of a flame is materially affected by the press

sphere in which it burns, a diminution of pressure causing a loss of inating power. If the light of a given flame burning in the air when arometer stands at 30 inches be represented by 100, each diminution ie inch in the height of the barometer will reduce the luminosity ve; and conversely, when the barometer rises one inch, the lumino- will be increased by five. This is not due to any difference in the of burning, which remains pretty constant, but to the more complete penetration of the rarefied air and the gases composing the flame, g rise to the separation of a smaller quantity of incandescent carbon. ir at a pressure of 120 inches of mercury, the flame of alcohol is ly luminous, the high density of the air discouraging the intermixture ie flame-gases with it, and thus allowing the separation of a portion rbon.

considering the influence exerted by the composition of the fuel the character of its flame, it will be necessary to bear in mind that kinds of fuel consist of carbon and hydrogen only, whilst others ain a considerable proportion of oxygen.

he following table exhibits the composition of some of the principal tances concerned in producing ordinary illuminating flames:—

Fuel.	Formula.	Carbon.	Hydrogen.	Oxygen.
rsh-gas,	C_2H_4	30	10	
fiant gas,	C_4H_4	60	10	
affine,	C_xH_x	60	10	
rpentine,	$C_{20}H_{16}$	75	10	
nzole,	$C_{12}H_6$	120	10	
ax,	$C_{92}H_{92}O_4$*	60	10	3·5
arine,	$C_{114}H_{110}O_{12}$	62·1	10	8·7
ine,	$C_{114}H_{104}O_{12}$	65·8	10	9·2
ohol,	$C_4H_6O_2$	40	10	27
od naphtha,	$C_2H_4O_2$	30	10	40

t may be stated generally that when the number of equivalents of on is less than that of hydrogen, the flame will be free from smoke, n the case of marsh-gas. When there are as many equivalents of on as of hydrogen, as in olefiant gas and paraffine, the flame is very le to smoke, unless managed with great judgment. Those hydro- ons which contain, like turpentine and benzole, a larger number of valents of carbon than of hydrogen, always burn with much smoke, require special contrivance to render them applicable for illuminating poses. Thus, camphine (turpentine) must be burnt in lamps with tall ow chimneys of peculiar construction to a strong current of air. zole (coal-naphtha) vapour must be mixed if it is required to with a smokeless flame.

a piece of cotton wool, moistened with ben flask provided two tubes (fig. 105), it will be found, on g by dipping o hot water, and blowing through one of th of benzole ur and air issuing from the other tube bright

* This is the composition of myricine, which

If coal-gas, which is essentially a mixture of hydrogen, marsh-gas olefiant gas, and generally contains rather too much hydrogen in p tion to its carbon, be enriched with carbon by ing over benzole (light coal naphtha), it burn a far more luminous flame (*naphthalised gas*)

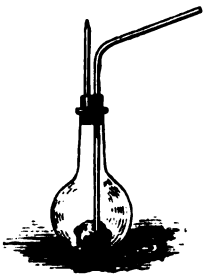


Fig. 105.

When the fuel contains oxygen, the carbo exist in larger proportion to the hydrogen w giving rise to the production of smoke, sinc oxygen will dispose of a portion of the c during the combustion. Thus, wax is muc liable to smoke than paraffine, although cont the same proportions of carbon and hyd whilst stearine (the chief part of tallow) and (forming the bulk of oils) may be burnt in nary candles and lamps, although still rich carbon, because they contain more oxygen als

Alcohol yields a flame of no illuminating value, although it co more carbon in proportion to its hydrogen than is present in mars because its oxygen helps to consume the carbon during the combu and prevents it from separating in the incandescent state. By a about one-tenth of its bulk of benzole or turpentine, however, a may be made to burn with a brilliant flame.

75. *The blowpipe flame.*—The principles already laid down render the structure of the blowpipe flame easily intelligible. It be remembered that in using the blowpipe, the stream of air is no pelled from the lungs of the operator (where a great part of its o would have been consumed), but simply from the mouth, by the c of the muscles of the cheeks. The first apparent effect upon the is entirely to destroy its luminosity, the free supply of air effectin immediate combustion of the carbon. The size of the flame, moreo much diminished, and the combustion being concentrated into a sr space, the temperature must be much higher at any given point c flame. In structure, the blowpipe flame is similar to the ordinary f consisting of three distinct cones, the innermost of which (A, fig. 1

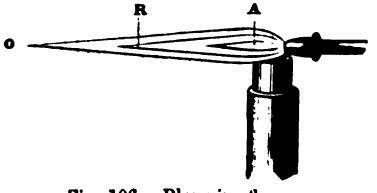


Fig. 106.—Blowpipe flame.

filled with the cool mixture and combustible gas. The s cone, especially at its point termed the *reducing* flame, f supply of oxygen at that part sufficient to convert the carbo carbonic acid, but leaves it a bonic oxide, which speedily re almost all metallic oxides pla that part of the flame to the me

state. The outermost cone (O) is called the *oxidising* flame, for the supply of oxygen from the surrounding air is unlimited, and any subs prone to combine with oxygen at a high temperature is oxidised exposed to the action of that portion of the flame; the hottest po the blowpipe flame, where neither fuel nor oxygen is in excess, ap to be a very little in advance of the extremity of the second (redu cone. The difference in the operation of the two flames is readily s

placing a little red lead (oxide of lead) in a shallow cavity

upon the surface of a piece of charcoal (fig. 107), and directing the flames upon it in succession; the inner flame will reduce a globule of metallic lead, which may be re-converted into oxide by exposing it to the outer flame.* The immense service rendered by this instrument to the chemist and mineralogist is well known.

Fig. 107.—Reduction of metals on charcoal.

By forcing a stream of oxygen through a flame from a gas-holder or bag, an intensely hot blowpipe flame is obtained, in which pipe-clay and platinum may be melted, and iron burns with great brilliancy (see fig. 48).

76. *Determination of the composition of gases containing carbon and hydrogen.*—In order to ascertain the proportions of carbon and hydrogen present in a gas, a measured volume of the gas is mixed with an excess of oxygen, the volume of the mixture carefully noted, and explosion determined by passing the electric spark; the gas remaining after the explosion is measured and shaken with potash, which absorbs the carbonic acid, from the volume of which the proportion of carbon may be calculated. For example,

	0·4	cubic inch of	marsh-gas, mixed with
	1·0	,,	oxygen, and exploded, left
	0·6	,,	gas; shaken with potash
it left	0·2	,,	oxygen.

Showing that 0·4 cubic inch of carbonic acid had been produced. This quantity of carbonic acid would contain 0·4 cubic inch of (imaginary) carbon vapour, and 0·4 cubic inch of oxygen. Deducting this last from the total amount of oxygen consumed (0·8 cubic inch), we have 0·4 cubic inch for the volume of oxygen consumed by the hydrogen. Now, 0·4 cubic inch of oxygen would combine with 0·8 cubic inch of hydrogen, which represents therefore the amount of hydrogen in the marsh-gas employed. It has thus been ascertained that

4 volumes of marsh-gas contain
4 volumes of (hypothetical) carbon vapour, and
8 volumes of hydrogen.

Fig. 108.
a eudiometer.

For the purpose of illustration, the analysis of marsh-gas may be effected in a Ure's eudiometer (fig. 108), but a considerable excess of oxygen should be added to moderate the explosion. The eudiometer having been filled with water, 0·1 cubic inch of marsh-gas is introduced into it, as described at p. 34, and having been transferred to the closed limb and accurately measured after equalising the level of the water, the open limb is again filled up with water, the eudiometer inverted in the trough, and 1·2 cubic inch of oxygen added; this is a

- the closed

allowing
figure, a
which

* By directing the reducing flame upon the metallic as
the oxidising flame to sweep over the surface of the cha
yellow incrustation of oxide of lead is formed upon the
affords additional evidence of the nature of the metal.

limb and carefully measured. The electric spark is then passed through the mixture (see p. 84), the open limb being closed by the thumb. The level of the water in both limbs is then equalised, and the volume of gas measured. The open limb is then filled up with a strong solution of potash, and closed by the thumb, so that the gas may be transferred from the closed to the open limb and back, until its volume is no longer diminished by the absorption of carbonic acid. The volume of residual oxygen having been measured, the calculation is effected as above described.

The results are more exact when the eudiometer is filled with mercury instead of water.

The following table exhibits the composition by volume of acetylene, marsh-gas, and olefiant gas (8 parts by weight of oxygen being considered to occupy one volume) :—

	Eqt. Weight.	Eqt. Volume.	Carbon Vapour.	Hydrogen.
Acetylene, C_4H_2	26	4 vols.	8 vols. ?	4 vols.
Marsh-gas, C_2H_4	16	4 „	4 „ ?	8 „
Olefiant gas, C_4H_4	28	4 „	8 „ ?	8 „

Coal-Gas.

77. The manufacture of coal-gas is one of the most important applications of the principle of destructive distillation, and affords an excellent example of the tendency of this process to develope new arrangements of the elements of a compound body. The action of heat upon coal, in a vessel from which air is excluded, gives rise to the production of a very large number of compounds containing some two or more of the five elements of the coal, in different proportions, or in different forms of arrangement. Although no clue has yet been obtained to indicate the true arrangement of these elements in the original coal (or, as it is termed, the *constitution* of the coal), it is certain that these various compounds do not exist in it before the application of heat, but are really the results of its action, that they are indeed *products* and not *educts*.

The most important forms assumed by the carbon and hydrogen when coal is strongly heated, are,—

Gases { Hydrogen. / Marsh-gas, C_2H_4 / Olefiant gas, C_4H_4 / Acetylene, C_4H_2 / Oil-gas, C_5H_5 } Liquids { Benzole, $C_{12}H_6$ / Toluole, $C_{14}H_8$ } Solids { Naphthaline, $C_{20}H_8$ / Anthracene, $C_{28}H_{10}$ / Paraffine, C_nH_n / *Coke*, C }

The nitrogen of the coal reappears in the fo

Gases { Nitrogen. / Ammonia, . . NH_3 }
Liquids { Aniline, . . $C_{12}H$ / Quinoline, . $C_{18}H$ / Hydrocyanic acid, C_2H }

The oxygen contributes to the production of—

Gases	Carbonic oxide,	CO	Liquids	Water, .	HO
	Carbonic Acid,	CO_2		Acetic acid,	$C_4H_3O_4$
				Carbolic acid,	$C_{12}H_6O_2$

Sulphur is found among the products as,

Sulphuretted hydrogen gas,	HS	Liquid (very volatile).	Bisulphide of carbon, CS_2

The illuminating gas obtained from coal consists essentially of free hydrogen, marsh-gas, olefiant gas, and carbonic oxide, with small quantities of acetylene, benzole vapour, and some other substances.

A fair general idea of its composition is given by the following table :—

Gas from Cannel Coal.

Hydrogen,	45·6 volumes.
Marsh-gas,	34·9 ,,
Carbonic oxide,	6·6 ,,
Olefiant gas,	4·0 ,,
Carbonic acid,	3·7 ,,
Oil-gas,	2·4 ,,
Nitrogen,	2·5 ,,
Sulphuretted hydrogen,	0·3 ,,
	100·0

The only constituents which contribute directly to the illuminating value of the gas are the marsh-gas, olefiant gas, oil-gas (acetylene, and benzole vapour).

The most objectionable constituent is the sulphur present as sulphuretted hydrogen and bisulphide of carbon, for this is converted by combustion into sulphuric acid, which seriously injures pictures, furniture, &c. The object of the manufacturer of coal-gas is to remove, as far as possible, everything from it, except the constituents mentioned as essential, and at the same time to obtain as large a volume of gas from a given weight of coal as is consistent with a good illuminating value.

The mode of purifying the gas, and the general arrangements for its manufacture, will be described in a later part of the work.

109.—Destructive distillation of coal.

f coal may be exhibited with the arrangement repre-
d liquid products (tar, ammoniacal liquor, &c.) are
ver (A). The first bent tube contains, in one
mper to de ia; and in the other (C)

a piece of paper impregnated with acetate of lead, which will be blackened by the sulphuretted hydrogen. The second bent tube (D) contains enough lime-water to fill the bend, which will be rendered milky by the carbonic acid. The gas is collected over water, in the jar E, which is furnished with a jet from which the gas may be burnt when forced out by depressing the jar in water.

Fig. 110.

The presence of acetylene in coal-gas may be shown by passing the gas from the supply-pipe (A, fig. 110), first through a bottle (B) containing a little ammonia, then through a bent tube (C), with enough water to fill the bend, and a piece of bright sheet copper immersed in the water in each limb. After a short time the bright red flakes of the acetylide of copper will be seen in the water.

SILICON.

78. In many of its chemical relations to other bodies this element will be found to bear a great resemblance to carbon; but whilst carbon is remarkable for the great variety of compound forms in which it is met with in nature, silicon is always found in combination with oxygen, as silicic acid, or silica (SiO_2), either alone or united with various metallic oxides, with which it forms *silicates*.

Silica.—The purest natural variety of silica is the transparent and colourless variety of quartz known as *rock crystal*, the most widely diffused ornament of the mineral world, often seen crystallised in beautiful six-sided prisms, terminated by six-sided pyramids (fig. 111), which are always easily distinguished by their great hardness, scratching glass almost as readily as the diamond. Coloured of a delicate purple, probably by a little organic matter, these crystals are known as *amethyst;* and when of a brown colour, as *Cairngorm stones* or *Scotch pebbles*. Losing its transparency and crystalline structure, we meet with silica in the form of *chalcedony* and of *carnelian*, usually coloured, in the latter, with oxide of iron.

Fig. 111.—Crystal of quartz.

Hardly any substance has so great a share in the lapidary's art as silica, for in addition to the above instances of its value for ornamental purposes, we find it constituting *agate*, *cat's eye*, *onyx*, so much prized for cameos, *opal*, and some other precious stones. In opal the silica is combined with water.

Sand, of which the whiter varieties are nearly pure silica, appears to have been formed by the disintegration of siliceous rocks, and has generally a yellow or brown colour, due to the presence of oxide of iron.

The resistance offered by silica to all impressions has become proverbial in the case of *flint*, which consists essentially of that substance coloured with some impurity. Flints are generally found in compact masses, distributed in regular beds throughout the chalk formation; their hardness, which even exceeds that of quartz, formerly rendered them useful for striking sparks with steel, by detaching small particles of the metal, which are so heated by the percussion as to continue to burn (see p. 10) in the air, and to inflame tinder or gunpowder upon which they are allowed to fall.

The part taken by silica in natural operations appears to be chiefly a mechanical one, for which its stability under ordinary influences peculiarly fits it, for it is found to constitute the great bulk of the soil which serves as a support and food-reservoir of land-plants, and enters largely into the composition of the greater number of rocks.

But that this substance is not altogether excluded from any share in life is shown by its presence in the shining outer sheath of the stems of the grasses and cereals, particularly in the hard external coating of the Dutch rush used for polishing; and this alone would lead to the inference that silica could not be absolutely insoluble, since the capillary vessels of plants are known to be capable of absorbing only such substances as are in a state of solution. Many natural waters also present us with silica in a dissolved state, and often in considerable quantity, as, for example, in the Geysers of Iceland, which deposit a coating of silica upon the earth around their borders.

Pure water, however, has no solvent action upon the natural varieties of silica. The action of an alkali is required to bring it into a soluble form.

To effect this upon the small scale, a few crystals of common washing-soda (carbonate of soda) may be powdered and dried; a little of the dried powder is placed upon a piece of platinum foil slightly bent up (fig. 112),

Fig. 112.—Fusion on platinum foil.

and is fused by directing the flame of a blowpipe upon the under side of the foil. As soon as the carbonate of soda is perfectly liquefied, a small quantity of very finely powdered white sand is thrown into it, when brisk effervescence will be observed, and the particles of sand will dissolve; fresh portions of sand may now be added as long as they produce effervescence, which is due to the escape of the carbonic acid, and since, in general, one acid can only be displaced by another, it is but reasonable to infer that the sand really possesses acid properties, and hence the fitness of its chemical name, *silicic acid*.

The piece of platinum foil with the melted mass upon it may now be placed in a little warm water, and allowed to soak for some time, when it will gradually dissolve, forming a solution of *silicate of soda*. This solution will be found decidedly alkaline to test-papers; for silicic acid, like carbonic, is too feeble an acid to neutralise entirely the alkaline properties of the soda.

If a portion of the solution of silicate of soda in water be poured into a test-tube, and two or three drops of hydrochloric acid added to it with occasional agitation, effervescence will be produced by the expulsion of *any carbonic acid still remaining, and the* solution will be converted into

a gelatinous mass by the separation of hydrated silicic acid. But if another portion of the solution of silicate of soda be poured into an excess of dilute hydrochloric acid (*i.e.*, into enough to render the solution distinctly acid), the silicic acid will remain dissolved in the water, together with the chloride of sodium formed by the action of the hydrochloric acid upon the soda.

In order to separate the chloride of sodium from the silicic acid, the process of *dialysis** must be resorted to.

Dialysis is the separation of dissolved substances from each other by taking advantage of the different rates at which they pass through moist diaphragms or *septa*.

If the mixed solution of chloride of sodium and silicic acid were poured upon an ordinary paper filter, it would pass through without alteration; but if parchment paper be employed, which is not pervious to water, although readily moistened by it, none of the liquid will pass through. If the cone of parchment paper be supported upon a vessel filled with distilled water (fig. 113), so that the water may be in contact with the outer surface of the cone, the hydrochloric acid and the chloride of sodium will pass through the substance of the parchment paper, and the water charged with them may be seen descending in dense streams from the outside of the cone. After a few hours, especially if the water be changed occasionally, the whole of the hydrochloric acid and chloride of sodium will have passed through, and a pure solution of silicic acid in water will remain in the cone.

Fig. 113.

This solution of silicic acid is very feebly acid to blue litmus paper, and not perceptibly sour to the taste. It has a great tendency to set into a jelly in consequence of the sudden separation of hydrated silicic acid. If it be slowly evaporated in a dish, it soon solidifies; but, by conducting the evaporation in a flask, so as to prevent any drying of the silicic acid at the edges of the liquid, it may be concentrated until it contains 14 per cent. of silicic acid. When this solution is kept, even in a stoppered or corked bottle, it sets into a transparent gelatinous mass, which gradually shrinks and separates from the water. When evaporated, *in vacuo*, over sulphuric acid, it gives a transparent lustrous glass which is composed of 22 per cent. of water and 78 per cent of silicic acid ($HO.SiO_2$).

This hydrate of silica cannot be redissolved in water, and is only soluble to a slight extent in hydrochloric acid. If it be heated to expel the water, the anhydrous silicic acid which remains is insoluble both in water and in hydrochloric acid, but is dissolved when boiled with solution of potash or soda, or their carbonates.

Silicic acid in the naturally crystallised form, as rock crystal and quartz, is insoluble in boiling solutions of the alkalies, and in all acids except hydrofluoric; but amorphous silica (such as that found at Farnham) is readily dissolved by boiling alkalies. These represent, in fact, two distinct modifications of silica. A transparent piece of rock crystal may be heated to bright redness without change, but if it be powdered previously to being heated, its specific gravity is diminished from 2·6 to 2·4, and it becomes soluble in boiling alkalies, having been converted into the amorphous modification.

* From διαλύω, to part asunder.

Crystals of quartz have been obtained artificially by the prolonged ion of water upon glass at a high temperature under pressure. When ed with the oxyhydrogen blowpipe, silica does not crystallise, being is converted into the amorphous variety of sp. gr. 2·3.

To prepare the amorphous modification of silica artificially, white sand in very powder may be fused, in a platinum crucible, with six times its weight of a mix- of equal weights of carbonate of potash and carbonate of soda, the mixture being re easily fusible than either of the carbonates separately. The crucible may be ted over a gas-burner supplied with a mixture of gas and air, or may be placed in ttle calcined magnesia contained in a fire-clay crucible, which may be covered up l introduced into a good fire. The platinum crucible is never heated in direct tact with fuel, since the metal would become brittle by combining with carbon, con, and sulphur derived from the fuel. The magnesia is used to protect the pla- um from contact with the clay crucible. When the action of the silicic acid upon alkaline carbonates is completed, which will be indicated by the cessation of the rvescence, the platinum crucible is allowed to cool, placed in an evaporating dish, l soaked for a night in water, when the mass should be irely dissolved. Hydrochloric acid is then added to solution, with occasional stirring, until it is distinctly d to litmus paper. On evaporating the solution, it will, certain point, solidify to a gelatinous mass of hydrated cic acid, which would be spirted out of the dish if poration over the flame were continued. To prevent , the dish is placed over an empty iron saucepan (fig. 1), so that the heat from the flame may be equally tributed over the bottom of the dish. When the mass quite dry the dish is allowed to cool, and some water poured into it, which dissolves the chlorides of potas- m and sodium (formed by the action of the hydro- oric acid upon the silicates of potash and soda), and es the silicic acid in white flakes. These may be lected upon a filter (fig. 115), and washed several times with distilled water. filter is then carefully spread out upon a hot iron plate, or upon a hot brick, and owed to dry, when the silicic acid is as a dazzling white powder, which st be strongly heated in a porcelain platinum crucible to expel the last es of water. It is remarkable for extreme lightness, especially when ted, the slightest current of air easily wing it away.

Fig. 114.

79. For effecting such fusions as that described, an air-gas blow-pipe (A, 116) supplied with air from a double on bellows (B), worked by a treadle (C), l be found most convenient. Where is not at hand, the fusion may be cted in a small furnace (fig. 117) sur- unted with a conical chimney, and fed h charcoal.

80. *Silicates.*—The acid proper- s of silicic acid are so feeble that is a matter of great difficulty to ermine the proportion of any e which is required to unite with in order to form a chemically utral salt. Like carbonic acid, it does not d on test-papers, and we are, therefore, dep *ining the proportion of alkali which neutra*

ecipitate.

he alkalies l of ascer- sense. In

attempting to ascertain the quantity of alkali with which it combines from that of the carbonic acid which it expels when heated with an alkaline carbonate, it is found that the proportion of carbonic acid expelled varies considerably, according to the temperature and the proportion of alkaline carbonate employed, probably because the attractions of silicic and carbonic acids for the alkaline bases are pretty evenly balanced.

By heating silicic acid with hydrate of soda (NaO . HO), it is found that 30 parts of silicic acid expel 18 parts of water, however much hydrate of soda is employed, and the same proportion of water is expelled from hydrate of baryta (BaO . HO) when heated with silicic acid.

According to the table at page 2, the formula SiO_2 represents 30 parts by weight of silicic acid, and 18 parts represent two equivalents of water which were combined in the hydrates with two equivalents of soda and baryta respectively. Hence it would appear that one equivalent of silicic acid is disposed to combine with two equivalents of an alkali, and since it is found that several of the crystallised mineral silicates contain two equivalents of a basic protoxide (MO) combined with one equivalent of silicic acid, it is usual to represent it as a *bibasic* acid, that is, an acid requiring two equivalents of an alkali to form a chemically neutral salt.

The circumstance that silicic acid is not capable of being converted into vapour at a high temperature, enables it to expel from their combinations with bases many other acids which, at ordinary temperatures, are able to displace silicic acid. Thus, sulphuric acid has a far more powerful attraction for bases than silicic acid, at the ordinary temperature, but when a mixture of silicic acid with a sulphate is strongly heated, the tendency of the sulphuric acid to assume the vaporous state at this temperature determines the decomposition of the sulphate and the formation of a silicate.

Fig. 116.—Air-gas blowpipe table.

The silicates form by far the greatest number of minerals. The different varieties of clay consist of silicate of alumina ; feldspar is a silicate of alumina and potash ; meerschaum is a silicate of magnesia.

The different kinds of glass are composed of silicates of potash, soda, lime, oxide of lead, &c.

None but the silicates of the alkalies are soluble in water.

81. *Silicon* or *Silicium*.—From the remarkably unchangeable character of silica, it is not surprising that it was long regarded as an elementary substance. In 1813, however, Davy succeeded in decomposing it by the action of potassium, and in obtaining an impure specimen of silicon. It has since been produced, far more easily, by converting the silicic acid into silico-fluoride of potassium ($KF . SiF_2$), and decomposing this at a high temperature with potassium or sodium, which combines with the fluorine to form a salt capable of being dissolved out by water, leaving

the silicon in the form of a brown powder (*amorphous silicon*) which resists the action of all acids, except hydrofluoric, which it decomposes, forming fluoride of silicon and evolving hydrogen ($Si + 2HF = SiF_2 + H_2$). It is also dissolved by solution of hydrate of potash, with evolution of hydrogen, and formation of silicate of potash. It burns brilliantly when heated in oxygen, but not completely, for it becomes coated with silica which is fused by the intense heat of the combustion. When heated with the blowpipe on platinum foil, it eats a hole through the metal, with which it forms the fusible silicide of platinum.

Fig. 117.—Charcoal furnace.

If silico-fluoride of potassium be fused with aluminum, a portion of the latter combines with the fluorine, and the remainder combines with the silicon, forming a silicide of aluminum. By boiling this with hydrochloric and hydrofluoric acids in succession, the aluminum is extracted, and crystalline scales of silicon, with a metallic lustre resembling black lead, are left (*graphitoid silicon*). In this form the silicon has a specific gravity of about 2·5, and refuses to burn in oxygen, or to dissolve in hydrofluoric acid. A mixture of nitric and hydrofluoric acids, however, is capable of dissolving it. Like graphite, this variety of silicon conducts electricity, though amorphous silicon is a non-conductor. The amorphous silicon becomes converted into this incombustible and insoluble form under the action of intense heat. It is worthy of remark that the combustibility of amorphous carbon (charcoal) is also very much diminished by exposure to a high temperature.

Unlike carbon, however, silicon is capable of being fused at a temperature somewhat above the melting point of cast iron; on cooling it forms a brilliant metallic-looking mass, which may be obtained, by certain processes, crystallised in octahedra so hard as to scratch glass like a diamond.

In their chemical relations to other substances there is much resemblance between silicon and carbon. They both form feeble acids with oxygen, which correspond in composition. Silicon, however, is capable of displacing carbon from carbonic acid, for if carbonate of potash be fused with silicon, the latter is dissolved, forming silicate of potash, and carbon is separated. Silicon also resembles carbon in its disposition to unite with certain metals to form compounds which still retain their metallic appearance. Thus silicon is found together with carbon in cast iron, and it unites directly with aluminum, zinc, and platinum, to form compounds resembling metallic alloys. Nitrogen enters into direct union with silicon at a high temperature, though it refuses to unite with carbon except in the presence of alkalies. In their relation to hydrogen, these two elements are widely different, for silicon is only known to form one compound with hydrogen, and that of a very unstable character.

The *hydride of silicon* has never yet been obtained in a perfectly pure state, but its composition is believed to correspond with the formula SiH. It derives its interest chiefly from the property of taking fire spontaneo in contact with the air, in which it burns with a brilliant white giving off clouds of silica, and depositing a brown film of silicon *cold surface.*

The impure hydride of silicon is prepared by decomposing silicide of mag with dilute hydrochloric acid. The silicide of magnesium is obtained by chloride of magnesium (MgCl) with silico-fluoride of sodium (NaF . SiF metallic sodium, when the latter combines with the chlorine and fluorine, l the magnesium free to unite with the silicon.

The chloride of magnesium may be prepared by dissolving ordinary carbo magnesia in hydrochloric acid, adding three parts of chloride of ammonium f part of carbonate of magnesia, evaporating to dryness in a porcelain dish, fus residue, and pouring it out on to a clean stone. Being very deliquescent it m kept in a well-closed bottle.

Silico-fluoride of sodium is made by neutralising hydro-fluosilicic acid wit bonate of soda, and evaporating to dryness.

To increase the fusibility of the mixture, some fused common salt will quired. Dried salt may be melted in a fire-clay crucible, at a bright red hea poured out upon a clean dry stone.

Forty parts of the chloride of magnesium, 35 of silico-fluoride of sodium fused chloride of sodium, and 20 of sodium in slices, are rapidly weighed, t together in a dry bottle, and thrown into a red-hot clay crucible, which i covered and heated as long as the yellow flame of sodium vapour is perce After cooling, the crucible is broken, when a dark-coloured layer of silicide o nesium will be found beneath a white layer of chloride and fluoride of sodium. T cide of magnesium must be rapidly detached, and preserved in a well-stopped

The silicide of magnesium is coarsely powdered, and introduced into a W bottle (fig. 118), provided with a funnel tube, and a short wide tube for deli the gas. The bottle is filled up with water (pre boiled to expel air, and allowed to cool), and pla the pneumatic trough (containing boiled wat that both bottle and tubes may remain filled water. A gas-jar, filled with boiled water, l been placed over the delivery-tube, some strong chloric acid is added through the funnel, gre being taken that no air shall enter. The hyd silicon is at once evolved, and must be allo stand over water for some little time, to al froth, caused by a slight separation of silica side. The gas may then be transferred to a jar, with a stop-cock, from which it may be a pass into the air for the examination of its fla

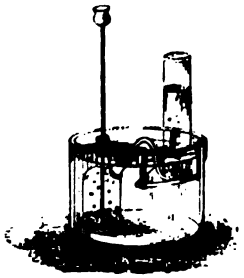


Fig. 118.

When cast iron, containing silicon, is bo hydrochloric acid until the whole of the ir solved, a grey frothy residue is left. If this be collected on a filter, w and dried, it is found to consist of black scales of graphite, mixed with a white powder. On boiling it with potash, hydrogen is evolved, and powder dissolves, forming a solution containing silicate of pot powder appears to be identical with a substance obtained by called *leucone*,* which is believed to have the composition S regarded as a hydrate of protoxide of silicon, 3SiO . 2HO. of potash would be explained by the equation

$$Si_3H_2O_5 + HO + 6KO = 3(2KO . SiO_2) +$$

Leucone is slowly converted into silicic acid, even by the gen being disengaged.

Another compound, containing silicon, hydrogen, and oxy *silicone*. It is a yellow substance, the general characters of w the compound last described. W d, under water, light, hydrogen is evolved, and th omes conv

Combining weight of silico

8 parts by weight of oxygen silicic acid. If it be assumed gous to that of carbonic acid

e weight combining with $O_2 = 16$ parts of oxygen) would be 14·8. lore exact experiments have recently fixed the number at 14.

Some chemists represent silicic acid as SiO_3, when the combining eight of silicon (or the weight combining with $O_3 = 24$ parts of oxygen) ould be 22·2 ($7·4 \times 3$), or by the more exact experiments, 21.

The *atomic weight* of silicon is generally represented by the number 8, though here, as in the case of carbon, theoretical considerations are elied upon, since the specific gravity of vapour of silicon cannot be ascer-ained by experiment.

The atomic formula of silicic acid would then be SiO_2, representing 28 arts of silicon, combined with 32 parts of oxygen, forming 60 parts of ilicic acid.

BORON.

82. Closely allied to silicon is another element, boron, which has at present never been found in animal or vegetable bodies, but appears to be entirely confined to the mineral kingdom.

Boracic acid.—A saline substance called *borax* ($NaO . 2BO_3 + 10Aq.$), has long been used in medicine, in working metals, and in making imitations of precious stones; this substance was originally imported from India and Thibet, where it was obtained in crystals from the waters of certain lakes, and came into this country under the native designation of *tincal*, consisting of impure borax, surrounded with a peculiar soapy substance, which the refiner of borax makes it his business to remove.

In 1702, in the course of one of those tentative experiments to which, though empirical in their nature, scientific chemistry is now so deeply indebted, Homberg happened to distil a mixture of borax and green vitriol (sulphate of iron), when he obtained a new substance in pearly plates, which was found useful in medicine, and received the name of *sedative salt*. A quarter of a century later, Lemery found that this substance might be separated from borax by employing sulphuric acid instead of sulphate of iron; but another quarter of a century elapsed before it was shown that in borax these pearly crystalline scales were combined with soda, and were possessed of acid properties which entitle them to retain the name *boracic acid*.

Until very recently this acid has been obtained in a free state from [illegible], and is now largely imported into this country from the [illegible] in the north of Italy, where it issues from the earth in [illegible] accompanied by violent jets of steam, which are [illegible] as *soffioni*. It would appear easy enough, [illegible] for the condensation of this steam, to obtain [illegible] companies it, but it is found necessary to cause [illegible] acid by passing it through water, for [illegible] (*lagunes*, fig. 119) are built up around [illegible] with water from the neighbouring springs [illegible] to flow successively into the different [illegible] -livity for that purpose, and it thus [illegible] of boracic acid. The neces-[illegible] water, in order to obtain the [illegible] be a great obstacle to the [illegible] where fuel is very expen-

sive. In 1817, however, Larderello conceived the project of evaporati this water by the steam-heat afforded by the soffioni themselves, a several hundred tons of boracic acid are now annually produced in th manner. The evaporation is conducted in shallow leaden evaporati pans (A, fig. 119), under which the steam from the soffioni is conduct through the flues (F) constructed for that purpose. As the demand f boracic acid increased on account of the immense consumption of bor in the porcelain manufacture, the experiment was made, with success, boring into the volcanic strata, and thus producing artificial soffioni, yiel ing boracic acid.

The crystals of boracic acid, as imported from these sources, conta salts of ammonia and other impurities. They dissolve in about thr times their weight of boiling water, and crystallise out on cooling, sin they require 26 parts of cold water to dissolve them. These crystals a represented by the formula $3HO.BO_3$. If they are sharply heated in retort, they partly distil over unchanged, together with the water deriv from the decomposition of another part; but if they be heated to 212° only, they effloresce, and become converted into $HO.BO_3$. When th is further heated, the whole of the water passes off, carrying with it little boracic acid, and the acid fuses to a glass, which remains perfect

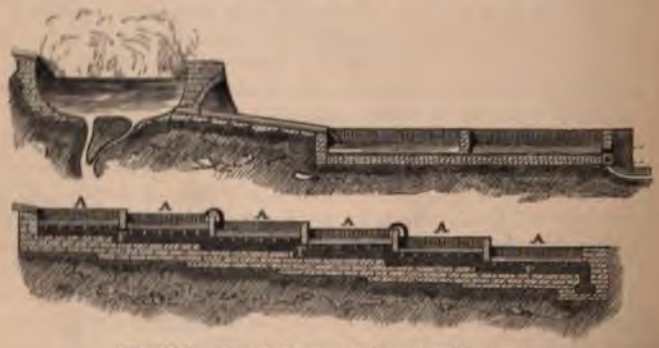


Fig. 119.—Boracic lagune and evaporating pans.

transparent on cooling (*vitreous boracic acid*). This anhydrous borac acid is slowly volatilised by the continued action of a very high temper ture. It dissolves very slowly in water.

A characteristic property of boracic acid is that of impart colour to flames. Its presence may thus be detected in the from a boiling solution of boracic acid in water, for if a spir or a piece of burning paper, be held in the steam, the flame a green tint, especially at the edges.

The colour is more distinctly seen when the crystallised boracic acid platinum foil in a spirit-flame or an air-gas and still better when are dissolved in boiling alcohol, and the solu boracic acid in borax may be ascertained by sulphuric acid to liberate the boracic acid, a mixture burn. Another peculiar property of If a piece of turmeric paper be dipped in a gentle heat, it assumes a fine brown-red colou *potash* or *its* carbonate. In applying this *fied with* hydrochloric acid, to set free the

Borates.—Boracic acid, like silicic, must be classed among the feeble acids. It colours litmus violet only, like carbonic acid, and does not neutralise the action of the alkalies upon test-papers. At high temperatures fused boracic acid dissolves the metallic oxides to form transparent glassy borates, which have, in many cases, very brilliant colours, and upon this property depend the chief uses of boracic acid in the arts.

Unlike the silicates, the borates are comparatively rare in the mineral world. No very familiar mineral substance contains boracic acid. A double borate of soda and lime, called *boro-natrocalcite*, is imported from Peru for the manufacture of borax; and the mineral known as *boracite* is a borate of magnesia.

In determining the proportion of base which boracic acid requires to form with it a chemically neutral salt, the same difficulties are met with as in the case of silicic acid (p. 105); but since it is found that 35 parts of boracic acid (the weight represented by BO_3) displace 27 parts of water (three equivalents) from hydrate of soda and from hydrate of baryta, both employed in excess, it would appear that the boracic acid requires three equivalents of a basic protoxide (MO) fully to satisfy its acid character, so that it is a *tribasic* acid, a conclusion which is supported by other evidence.

83. *Boron.*—It was in the year 1808 that Gay-Lussac and Thénard succeeded, by fusing anhydrous boracic acid with potassium, in extracting from it the element boron as an olive-green powder (*amorphous boron*), which has a general resemblance to silicon, but, unlike that element, may be oxidised by nitric acid. It also requires a higher temperature to fuse it than is required by silicon. The *graphitoid boron*, corresponding to the black-lead variety of carbon, is obtained in brilliant copper-coloured scales by a process similar to that which furnishes the graphitoid silicon.

The most remarkable form of boron is the crystallised variety or *diamond of boron*, which is obtained by very strongly heating amorphous boron with aluminum, and afterwards extracting the aluminum from the mass with hydrochloric acid. These crystals are brilliant transparent octahedra, which are sometimes nearly colourless, and resemble the diamond in their power of refracting light, and in their hardness, which is so great that they will scratch rubies, and will even wear away the surface of the diamond.* This form of boron cannot be attacked by any acid, but is dissolved by fused hydrates of the alkalies. The flame of the oxyhydrogen blowpipe does not fuse it, and it only undergoes superficial conversion into boracic acid when heated to whiteness in oxygen. When heated to [illegible] chlorine, however, it burns, forming chloride of boron. Boron [illegible] silicon in its chemical relations to the other elements. [illegible], to form a compound with hydrogen, and has a [illegible]bine with nitrogen than is manifested by silicon. [illegible]ly when heated to redness, forming a white [illegible] *nitride of boron* (BN).

[illegible]—According to the experiments of Davy, [illegible]combine with 3·76 parts of boron to form [illegible] borax, that one equivalent of soda (31 [illegible]ts of boracic acid. This would contain, [illegible]xygen [illegible]d if it be taken to represent

[illegible]m of the beaker-glass used in

one equivalent of boracic acid, that of boron would be (69·5 − 47·3 =) 22·2, and the formula of boracic acid would be BO_6 (representing 22·2 parts of boron and 48 parts of oxygen). There are reasons, however, for believing that borax really contains two equivalents of boracic acid, combined with one equivalent of soda, so that the equivalent of boron would be the half of 22·2, or 11·1 (by more exact experiments, 11), and boracic acid would be BO_3 (11 parts of boron with 24 parts of oxygen). The same number is generally taken for the *atomic weight* of boron, the atomic formula of boracic anhydride being written B_2O_3, and that of the crystallised acid $HBO_2 . H_2O$.

84. The elements carbon, boron, and silicon form a natural group, possessing many properties in common. They are all capable of existing in the amorphous, the graphitoid, and the crystalline forms; all incapable of being converted into vapour; all exhibit a want of disposition to dissolve; all form feeble acids with oxygen by direct union; and all unite with several of the metals to form compounds which resemble each other. Boron and silicon are capable of direct union with nitrogen, and so is carbon if an alkali be present. Recent researches attribute to silicon the power of occupying the place of carbon in some organic compounds, and the formulæ of leucone and silicon ($Si_3H_2O_5$ and $Si_6H_2O_4$) strongly remind us of the organic compounds of carbon with hydrogen and oxygen. In many of its physical and chemical characters, silicon is closely allied with the metals, and it will be found that tin and titanium bear a particular resemblance to it in their chemical relations.

NITROGEN.

85. This element, which has already been referred to as forming four-fifths of the volume of air, is elsewhere found in nature in the forms of saltpetre or nitrate of potash ($KO . NO_5$), and Chili saltpetre or nitrate of soda ($NaO . NO_5$). It also occurs as ammonia (NH_3) in the atmosphere and in the gaseous emanations from volcanoes. It is contained in the greater number of animal, and in many vegetable substances, and therefore has a most important share in the chemical phenomena of life.

Nitrogen is generally obtained by burning phosphorus in a portion of air confined over water (fig. 120.) The phosphorus is floated on the water in a small porcelain dish, kindled, and covered with a bell-jar. The nitrogen remains mixed with clouds of phosphoric acid (PO_5), which may be removed by allowing the gas to stand over water.

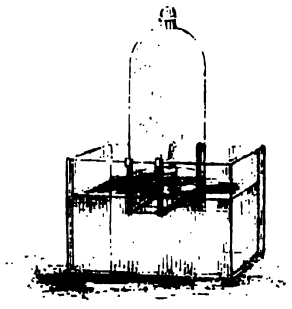


Fig. 120. Preparation of nitrogen.

When nitrogen is required in larger quantity, it is more conveniently prepared by passing air from a gas-holder over metallic copper heated to redness in a tube. The negative properties of this gas, however, are so very uninteresting, and render it so useless for most chemical purposes, that it will be unnecessary to give further details respecting its preparation. The remarkable chemical inactivity of free nitrogen has been alluded to in the *rticle on* atmospheric air. It has been seen, however, to be capable of

combining directly with boron and silicon, and magnesium and titanium unite with it even more readily at a high temperature. It is conspicuous among the elements for forming, with hydrogen, a powerful alkali (ammonia, NH_3), and with oxygen a powerful acid (nitric acid, NO_5), whilst the feeble chemical ties which hold it in combination with other elements, joined to its character of a permanent gas, render many of its compounds very unstable and explosive, as is the case with the so-called chloride and iodide of nitrogen, gun-cotton, the fulminates of silver and mercury, nitroglycerine, &c.

The discovery of nitrogen was made by Rutherford (Professor of Botany in the University of Edinburgh) in 1772, who was led to it by the observation, that respired air was still unfit to support life when all the carbonic acid had been absorbed from it by a caustic alkali. Hence the name *azote* (ἀ priv. and ζωὴ life) formerly bestowed upon this gas.

Ammonia.

86. The proportion of ammonia existing in atmospheric air is so small that it is difficult to determine it with precision; it appears, however, not to exceed one-hundredth of a grain in a cubic foot. This scarcity of ammonia in air is not to be accounted for by a scantiness in the supply, but rather by an excess in the demand; since ammonia is constantly sent forth into the air by the putrefaction of animal and vegetable substances containing nitrogen. Plants do not appear to be capable of absorbing from the atmosphere the nitrogen which it contains so abundantly in the uncombined form, but to derive their chief supply of that element from the ammonia, brought down by rain from the atmosphere, into which it is continually introduced from various sources. During the life of an animal, it restores to the air the nitrogen which formed part of its wasted organs, in part directly as ammonia in the breath and in the exhalation from the skin,* whilst another portion is separated as urea and uric acid in the urine, to be eventually converted into ammonia when the excretion undergoes putrefaction. Dead animal and vegetable matter when putrefying, restores its nitrogen to the air, chiefly in the forms of ammonia and substances closely allied to it, but partly also, it is said, in the free state.

The *liquor ammoniæ*, or solution of ammonia in water, which is so largely used in medicine and the arts, is obtained chiefly from the *ammoniacal liquor* resulting from the destructive distillation of coal for the manufacture of gas. The ammoniacal liquor of the gas-works contains ammonia in combination with carbonic and hydrosulphuric acids. As the first step towards extracting the ammonia in a pure state, the liquor is neutralised with hydrochloric acid, which combines with the ammonia, expelling the carbonic and hydrosulphuric acid gases. Since the latter has a very bad smell and is injurious to health, the neutralisation is generally effected in covered vats furnished with pipes, which [illegible] the gases into a furnace where the hydrosulphuric acid is burnt, [illegible]r and sulphurous acid. The solution of hydrochlorate of a[illegible]rated to expel part of the water, and allowed to cool in [illegible]ined with lead, where the hydrochlorate is deposited in [illegible]ntain a good

* Some doubt exists as to the exhalation of am[illegible] skin of man under normal conditions.

deal of tarry matter. These crystals are moderately heated in an ir to deprive them of tar, and are finally purified by *sublimation*, that converting them into vapour, and allowing this vapour to condense into the solid form. For this purpose th tals are heated in a cylindrical iron vessel c with an iron dome lined with fire-clay. The chlorate of ammonia rises in vapour below heat, and condenses upon the dome in the f the fibrous cake known as *sal-ammoniac* i merce.

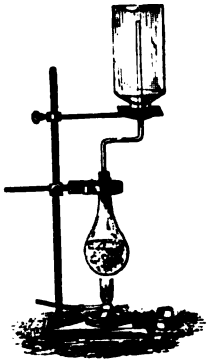


Fig. 121.—Preparation of ammonia.

To obtain ammonia from this salt, an ou it is reduced to coarse powder, and rapidly with two ounces of powdered quick-lime. mixture is gently heated in a dry Florenc (fig. 121), and the gas, being little more th as heavy as air (sp. gr. 0·59), may be co in dry bottles by displacement of air, the being allowed to rest upon a piece of tin which is perforated for the passage of the To ascertain when the bottles are filled, a p red litmus paper may be held at some little distance above the when it will at once acquire a blue colour if the ammonia escapes. bottles should be closed with greased stoppers.

The action of the lime upon hydrochlorate of ammonia is explai the following equation :—

$$NH_3.HCl + CaO = CaCl + HO + NH_3$$

Hydrochlor. amm. Lime. Chloride of calcium. Ammonia.

The readiest method of obtaining gaseous ammonia for the study of its ties consists in gently heating the strongest *liquor ammoniæ* in a retort or fl vided with a bent tube for collecting the gas by displacement (fig. 122). is evolved from the solution a low heat, and may be collec accompanied by steam.

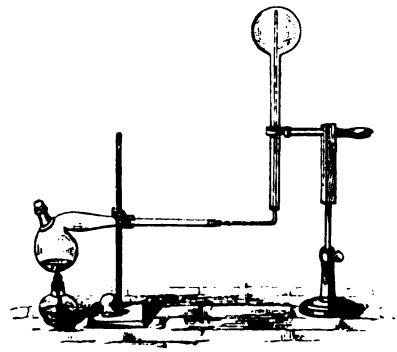


Fig. 122.

Ammonia is readily guished by its very charac smell, and its powerful a action upon red litmus a meric papers. It is absor water in greater proport volume than any other g volume of water absorbin than 700 volumes of an at the ordinary temperatu becoming one-and-a-half v of solution of ammonia of gravity 0·88. No chemica bination appears to take place between the water and ammonia, gas gradually escapes on exposing the solution to the air, and no compound of the two has been noticed. The escape of the ga the solution is attended with great production of cold, much h coming latent in the conversion of the ammonia from the liquid gaseous state.

The rapid absorption of ammonia by water is well shown by filling a

. 123) with the gas, placing it with its mouth downwards in a small capsule
ary which is placed in a large basin. If
n be filled with water, it cannot come into
with the ammonia until the mouth of the
raised out of the mercury, when the water
ckly enter and fill the flask. The water
e coloured with reddened litmus to exhibit
line reaction of the ammonia.

Fig. 123.

hibit the easy expulsion of the ammoniacal
a water by heat, a moderately thick glass
ut 12 inches long and half an inch in dia-
ay be nearly filled with mercury, and then
with strong solution of ammonia; on closing
he thumb and inverting it into a vessel of
(fig. 124) the solution will, of course, rise
e mercury to the closed end of the tube. By
this end of the tube in the hand, a con-
quantity of gas may be expelled, and the mercury will be depressed. If
ot water be poured over the top of the tube, the latter will become filled
moniacal gas, which will be absorbed again by the water when the tube is
to cool, the mercury re-
to fill the tube.

Fig. 124.

solution of ammonia,
is an article of com-
s prepared by conduct-
gas into water con-
n a two-necked bottle,
ond neck being con-
with a tube passing
other bottle containing
n which any escaping
ia may be condensed.
ength of the solution is
from its specific gra-
hich is lower in propor-
the quantity of am-
n the solution is greater.

at 57° F., a solution of
·8844 contains 36 parts by
of ammonia in 100 parts
ion; the sp. gr. 0·8976 in-
30 per cent.; 0·9106, 25 per cent.; 0·9251, 20 per cent.; 0·9414, 15 per
·9593, 10 per cent.; 0·979, 5 per cent. The specific gravity is ascertained by
ng the weights of equal volumes of water and of the
at the same temperature. For this purpose, a light
d bottle is provided, capable of containing about two
nces. This is thoroughly dried, and counterpoised in
ce by placing in the opposite pan a piece of lead, which
cut down to the proper weight. The bottle is then filled
ution of ammonia, the temperature observed with a ther-
r and recorded, the stopper inserted, and the bottle weighed.
n well rinsed out, filled with distilled water, the tempera-
ualised with that of the ammonia by placing the bottle
warm or cold water, and the weight ascertained as before.
cific gravity is obtained by dividing the weight of the solu-
ammonia by that of the water. The *ammonia-meter* (fig.
convenient instrument for rapidly ascertaining the specific
of liquids lighter than water. It consists of a hollow glass
th a long stem, weighted with a bulb containing shot or mer-
that when placed in distilled water it may sink to 1000° of the

Fig. 12

scale marked on the stem, this number representing the specific gravi When placed in a liquid lighter than water, it must, of course, sink lo to displace more liquid (since solids sink until they have displaced their of liquid). By trying it in liquids of known specific gravities, the ma scale to which it sinks may be made to indicate the specific gravity of The ammonia-meter generally has a scale so divided that it indicates per-centage weight of ammonia. In this country the specific gravity o always supposed to be taken at 62° F.

The common name for solution of ammonia, *spirit of har* derived from the circumstance that it was originally obtained cinal purposes by distilling shavings of that material.

When ammonia is exposed to a temperature of – 40° F. (*i.e.* the freezing-point), or to a pressure of 6½ atmospheres at 50°, it to a clear liquid, which solidifies at a temperature of – 103° F. crystalline mass. The compa with which it may be liquef to its application in Carré apparatus (fig. 126), in whi generated by heating a co solution of ammonia in a boiler (A) is liquefied by its sure in an iron receiver (B) cold water. When the boil off the fire and cooled in liquefied ammonia evaporat pidly from the receiver bac boiler, thereby producing so that a vessel of water placed (C) in the receiver is at once into ice. A refrigerator c upon this principle is emplo *salt gardens* of the south of France, in order to render their c operations independent of the temperature of the air.

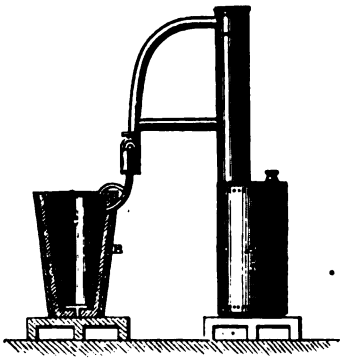


Fig. 126.—Carré's freezing apparatus.

The liquefaction of ammonia is very easily effected by heating the chloride of silver in one limb of a sealed tube, the other limb of which is freezing mixture. A piece of stout light green glass tube (A, fig. 12 inches long and half diameter, is drawn out inch from one end to a About 800 grains of chlo (dried at 400° F.) are int the tube, so as to lie l For this purpose a gut paper (B) should be cut loosely in the tube, the silver placed upon it, a has been thrust into th horizontally) the latter turned upon its axis, so t ride of silver may fall paper, which may then be The tube is now draw narrow neck at about a the other end, as in C, wards carefully bent, as being taken that none of the chloride of silver falls into the short limb which should be about four inches long. The tube is then supported *so that the long* limb may be horizontal, and is connected, by a tub

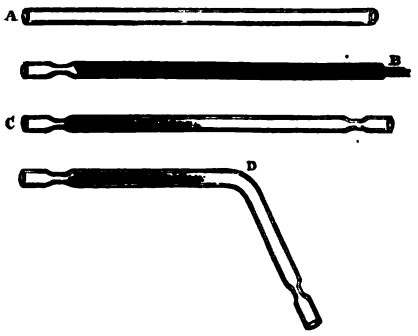


Fig. 127.

with an apparatus delivering dry ammonia, prepared by heating 1000 grains of sal-ammoniac with an equal weight of quick-lime in a flask, and passing the gas, first into an empty bottle (A, fig. 128) standing in cold water, and afterwards through a bottle (B) filled with lumps of quick-lime to absorb all aqueous vapour.

Fig. 128.

The long limb of the tube must be surrounded with filtering paper, which is kept wet with cold water. The current of ammonia should be continued at a moderate rate, until the tube and its contents no longer increase in weight, which will occupy about three hours—about 35 grains of ammonia being absorbed. The longer limb is sealed by the blowpipe flame whilst the gas is still passing, and then, as quickly as possible, the shorter limb, keeping that part of the tube which is occupied by the ammoniated chloride of silver still carefully surrounded by wet paper.

When the shorter limb of this tube (fig. 129) is cooled in a mixture of ice and salt (or of 8 ounces of sulphate of soda and 4 measured ounces of common hydrochloric acid), whilst the longer limb is gently heated from end to end by waving a spirit flame beneath it, the ammonia evolved by the heat from the ammoniated chloride of silver, which partly fuses, will condense into a beautifully clear liquid in the cold limb. When this is withdrawn from the freezing mixture, and the tube allowed to cool, the liquid ammonia will boil and gradually disappear entirely, the gas being again absorbed by the chloride of silver, so that the tube is ready to be used again.

Fig. 129.—Liquefaction of ammonia.

Ammonia is feebly combustible in atmospheric air, as may be seen by holding a taper just within the mouth of an inverted bottle of the gas, which burns with a peculiar livid flickering light around the flame, but will not continue to burn when the flame is removed. During its combustion the hydrogen is converted into water, and the nitrogen set free. In oxygen, however, ammonia burns with a continuous flame.

Fig. 130.

This is very well shown by surrounding a tube delivering a stream of ammonia (obtained by heating strong solution of ammonia in a retort) with a *much wider tube open at both ends (fig. 130)*, through which oxygen is passed by

holding the flexible tube from a gas-bag or gas-holder underneath it. On kindling the stream of ammonia it will give a steady flame of ten or twelve inches long.

A similar experiment may be made with a smaller supply of oxygen, by lowering the tube delivering ammonia into a bottle or jar of oxygen, and applying a light to it just as it enters the mouth of the jar (fig. 131).

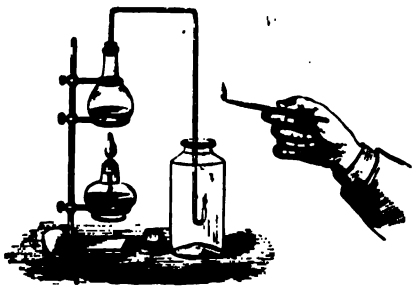


Fig. 131.

The elements of ammonia are easily separated from each other by passing the gas through a red-hot tube, or still more readily by exposing it to the action of the high temperature of the electric spark, when the volume of the gas rapidly increases until it is exactly doubled, one volume of ammonia being decomposed into $\frac{1}{2}$ volume of nitrogen and $\frac{3}{2}$ volumes of hydrogen.

For this experiment a measured volume of ammonia gas is confined over mercury (fig. 132), in a tube through which platinum wires are sealed for the passage of the spark from an induction-coil. The volume of the gas is doubled in a few minutes, and if the tube be furnished with a stop-cock (A), the presence of free hydrogen may be shown by filling the open limb with mercury and kindling the gas as it issues from the jet.*

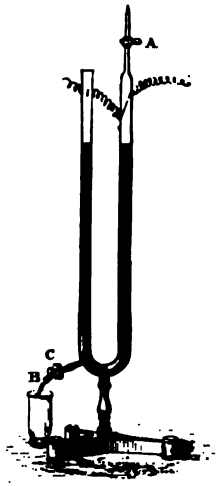


Fig. 132.

As might be expected from its powerfully alkaline character, ammonia exhibits a strong attraction for acids, which it neutralises perfectly. If a bottle of ammonia gas, closed with a glass plate, be inverted over a similar bottle of hydrochloric acid gas, and the glass plates withdrawn (fig. 133), the gases will combine, with disengagement of much heat, forming a white solid, the hydrochlorate of ammonia (NH_3. HCl), in which the acid and alkali have neutralised each other. Again, if ammonia be added to diluted sulphuric acid, the latter will be entirely neutralised, and by evaporating the solution, crystals of the sulphate of ammonia (NH_3. HO . SO_3) may be obtained.

The substances thus produced by neutralising the acids with solution of ammonia bear a strong resemblance to the salts formed by neutralising the same acids with solutions of potash and soda, a circumstance which would encourage the idea that the solution of ammonia must contain an alkaline oxide similar to potash or soda.

Berzelius was the first to make an experiment which appeared strongly to favour this view (commonly spoken of as the ammonium theory of Berzelius). The negative pole of a galvanic battery was placed in con-

* The eudiometer for passing electric sparks in rapid succession must have the platinum wires passed through the glass as shown in fig. 132, or it will be cracked by the heat of the sparks. The outlet tube B, closed by a small screw clamp C, pinching a caoutchouc connector, allows the mercury to be drawn off when necessary, to equalise the level in the *two limbs*.

ercury at the bottom of a vessel containing a strong solution of
ı which the positive pole of the battery was immersed. Oxygen
ged at this pole, whilst the mer-
tact with the negative pole swelled
five times its original bulk, and
soft solid mass, still preserving,
s metallic appearance. So far,
of the experiment resembles that
ıen hydrate of potash is decom-
similar circumstances, the oxygen
ıt the positive pole, and the potas-
negative, where it combines with
y. Beyond this, however, the
s not hold; for in the latter case
c potassium can be readily separ-

Fig. 133.

the mercury, whilst in the former, all attempts to isolate the
have failed, for the soft solid mass resolves itself, almost
y after its preparation, into mercury, ammonia (NH_3), and
ıne equivalent of the latter being separated for each equivalent
. This would also tend to support the conclusion, that a sub-
ng the composition $NH_3 + H$ or NH_4 had united with the
nd since the latter is not known to unite with any non-metallic
ithout losing its metallic appearance, it would be fair to con-
the soft solid was really an amalgam of ammonium. How-
ncrease in the weight of the mercury is so slight, and the
whether obtained by this or by other methods, is so unstable,
ld appear safer to attribute the swelling of the mercury to a
ange caused by the presence of the ammonia and hydrogen
is difficult to believe that the solution of ammonia does really
oxide of ammonium (NH_4O), when we find it evolving
o easily; but it is equally difficult, upon any other hypo-
xplain the close resemblance between the salts obtained by
acids with this solution, and those furnished by potash and

ary mode of exhibiting the production of the so-called *amalgam of ammo-* in acting upon the hydrochlorate of ammonia (NH_3. HCl), or *chloride of* H_4Cl), with the amalgam of sodium. A little pure mercury is heated , and a pellet of sodium thrown into it, when combination takes place nergy. When the amalgam is nearly cool it may be poured into a ontaining a moderately strong solution of chloride of ammonium; the once swells to many times its former bulk, forming a soft, solid sub- r than water, which may be shaken out of the tube as a cylindrical osing rapidly with effervescence, evolving ammonia and hydrogen, and ng its original volume and liquid condition.

bining weight and volume of ammonia.—It is found by experi- ne combining weight (36·5 grains) of hydrochloric acid requires f ammonia to effect complete neutralisation by combining with hydrochlorate of ammonia. This result being confirmed by s upon other acids, 17 is regarded as representing the combin- (or equivalent) of ammonia. This quantity of the gas occupies the volume of 8 parts by weight (one equivalent) of oxygen, so gas be taken as the unit of volume, the combining volume of rill be 4. Since the 17 parts by weight of ammonia occupy *olume of one part by weight* (one equivalent) of hydrogen, if

that gas be taken as the unit of volume, the combining volume of ammonia will be 2.

88. *Combining weight and volume of nitrogen.*—17 grains of ammonia have been proved to contain 14 grains of nitrogen combined with 3 grains of hydrogen. The latter gas being taken as the unit of combining weights, the 3 grains would represent 3 combining weights of hydrogen, and the question arises, How many combining weights of nitrogen are represented by the 14 grains? On referring to the composition of ammonia by volume, we find that it furnishes three volumes of hydrogen for one volume of nitrogen when decomposed by the electric spark (p. 118), and hence it seems reasonable to conclude that it contains one combining weight of nitrogen (14) and three combining weights of hydrogen (3), when the combining volume of nitrogen (or the volume occupied by its combining weight) will be equal to that of hydrogen.

It will also be seen hereafter that the hydrogen in ammonia can be replaced by other bodies *in thirds*, showing that there must be three atoms of hydrogen present, whilst the 14 parts of nitrogen cannot be replaced in fractions, so that it must represent a single atom.

The composition of ammonia by weight and volume is exhibited in the following table:—

		O = 1 vol.	H = 1 vol.	Parts by weight.
Nitrogen . . .	1 equivt.	2 vols.	1 vol.	14
Hydrogen . . .	3 equivts.	6 vols.	3 vols.	3
Ammonia . . .	1 equivt.	4 vols.	2 vols.	17

It will be seen that the atomic or molecular formula of ammonia, based upon the assumption that one volume of an element in the gaseous state represents one atom, coincides with its equivalent formula.

89. *Determination of nitrogen in organic substances.*—An exact knowledge of the composition of ammonia is of great importance, because the general method of ascertaining the proportion of nitrogen present in animal and vegetable substances consists in converting that element into ammonia, which, being collected and weighed, furnishes by calculation the weight of nitrogen present.

To ascertain the proportion of nitrogen present in an organic substance, a weighed quantity of it is mixed with a large proportion of *soda-lime* (a mixture of hydrate of soda and hydrate of lime), and introduced into a tube of German glass (A, fig. 134) to which is attached, by a perforated cork, a bulb apparatus (B) containing hydrochloric acid. On heating the tube inch by inch with a charcoal or gas furnace, the nitrogen of the substance is evolved in combination with the hydrogen of the hydrates, in the form of ammonia, which is absorbed by the hydrochloric acid in the bulbs. When the whole length of the tube has been heated, the point (C) is nipped off, and air drawn through by applying suction to the orifice (D) of the bulb apparatus, so that all the ammonia may be carried into the hydrochloric acid. Its weight is then ascertained, either by

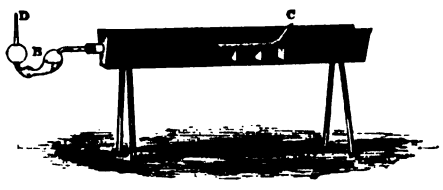


Fig. 134.—Estimation of nitrogen.

evaporating the liquid in a weighed dish placed over a steam bath, and weighing the hydrochlorate of ammonia, or more accurately by converting it into the double chloride of platinum and ammonium. Sometimes a solution of sulphuric acid of known strength is substituted for the hydrochloric acid in the bulbs, and the weight of the ammonia is ascertained by determining the quantity of acid which has been neutralised.

To illustrate the change which takes place when the organic substance is heated with the hydrates of soda and lime, let it be supposed that urea is the substance submitted to analysis.

$$C_2H_4N_2O_2 + NaO.HO + CaO.HO = NaO.CO_2 + CaO.CO_2 + 2NH_3$$

Urea.

The hydrate of soda alone would produce the same result, but would corrode the glass too rapidly.

In the analysis of an organic substance containing carbon, hydrogen, nitrogen, and oxygen, the proportions of carbon and hydrogen having been ascertained by the method described at p. 73, and that of nitrogen by the process given above, the sum of the carbon, hydrogen, and nitrogen is deducted from the entire weight of the substance to obtain the proportion of oxygen. The weights thus found are divided by the combining weights of the several elements to obtain the empirical formula, which is converted into a rational formula on the principle illustrated at p. 75.

For example, 10 grs. of urea were found to contain 2 grs. of carbon, 0·66 gr. of hydrogen, and 4·67 grs. of nitrogen.

10 grs. of urea *minus* 7·33 (carbon, hydrogen, and nitrogen) = 2·67 grs. of oxygen.

Dividing each of these numbers by the combining weight of the element to which it refers, we have,

2·0	÷ 6	= 0·33	of a combining weight of	carbon,
0·66	÷ 1	= 0·66	,,	,,	hydrogen,
4·67	÷ 14	= 0·33	,,	,,	nitrogen,
2·67	÷ 8	= 0·33	,,	,,	oxygen,

leading to the empirical formula $C_{33}H_{66}N_{33}O_{33}$, or in its simplest form, CH_2NO, for urea. But urea is an organic base, capable of uniting with acids to form salts, and it is found that to neutralise one combining weight (36·5 parts) of hydrochloric acid, 60 parts of urea are necessary. This quantity would contain 12 parts (two combining weights) of carbon, 4 parts (four combining weights) of hydrogen, 28 parts (two combining weights) of nitrogen, and 16 parts (two combining weights) of oxygen, so that the true formula for urea would be $C_2H_4N_2O_2$.

90. *Formation of ammonia in the rusting of iron.*—Although free nitrogen and hydrogen cannot be made to form ammonia by direct combination, this compound is produced when the nitrogen meets with hydrogen in the *nascent* state; that is, at the instant of its liberation from a combined form. Thus, if a few iron filings be shaken with a little water in a bottle of air, so that they may cling round the sides of the bottle, and a piece of red litmus paper be suspended between the stopper and the neck, it will be found to have assumed a blue colour in the course of a few hours, and ammonia may be distinctly detected in the rust which is produced. It appears that the water is decomposed by the iron, in the presence of the carbonic acid of the air and water, and that the hydrogen liberated enters at once into combination with the nitrogen, held in solution by the water, *to form ammonia.*

91. *Production of nitrous and nitric acids from ammonia.*—If a few drops of a strong solution of ammonia be poured into a pint bottle, and ozonised air (from the tube for ozonising by induction, fig. 10) be passed into the bottle, thick white clouds will speedily be formed, consisting of *nitrite of ammonia*, the nitrous acid having been produced by the oxidation of the ammonia at the expense of the ozonised oxygen—

$$2NH_3 + O_6 = \underset{\text{Nitrite of ammonia.}}{NH_3 . HO . NO_3} + 2HO$$

If copper filings be shaken with solution of ammonia in a bottle of air, white fumes will also be produced, together with a deep blue solution containing oxide of copper and nitrite of ammonia; the act of oxidation of the copper appearing to have induced a simultaneous oxidation of the ammonia.

Fig. 135.

A coil of thin platinum wire made round a pencil, if heated to redness at the lower end and suspended in a flask (fig. 135) with a little strong ammonia at the bottom, will continue to glow for a great length of time, in consequence of the combination of the ammonia with the oxygen of the air taking place at its surface, attended with great evolution of heat. Thick white clouds of nitrite of ammonia are formed, and frequently red vapour of nitrous acid (NO_3) itself.

If a tube delivering oxygen gas be passed down to the bottom of the flask (fig. 136), the action will be far more energetic, the heat of the platinum rising to whiteness, when an explosion of the mixture of ammonia and oxygen will ensue. After the explosion the action will recommence, so that the explosion will repeat itself as often as may be wished. It is unattended with danger if the mouth of the flask be pretty large. By regulating the stream of oxygen, the bubbles of that gas may be made to burn as they pass through the ammonia at the bottom of the flask.

Fig. 136.

In the presence of strong bases, and of porous materials to favour oxidation, ammonia appears to be capable of suffering further oxidation and conversion into nitric acid, which combines with the base to form a nitrate, thus—

$$NH_3 + CaO + O_8 = \underset{\text{Nitrate of lime.}}{CaO . NO_5} + 3HO$$

This formation of nitrates from ammonia is commonly referred to as *nitrification*, and appears to play an important part in the formation of the natural supplies of saltpetre which are of so great importance to the arts.*

Compounds of Nitrogen and Oxygen.

92. Though these elements in their pure state exhibit no attraction for each other, five compounds, which contain them in different proportions, have been obtained by indirect processes. The relative proportions of

* The charcoal which has been used in the sewer ventilators (see p. 59) has been found to contain abundance of nitrates.

oxygen in these compounds are exhibited in the following table, where the weight of nitrogen present is supposed to remain constant :—

Oxides of Nitrogen.

Name.	Equivalent Formula.	By Weight.	
		N	O
Nitrous oxide	NO	14	8
Nitric oxide	NO_2	14	16
Nitrous acid	NO_3	14	24
Nitric peroxide . . .	NO_4	14	32
Nitric acid	NO_5	14	40

When a succession of strong electric sparks from the induction coil is passed through atmospheric air in a flask (especially if the air be mixed with oxygen), a red gas is formed in small quantity, which is either nitrous acid (NO_3) or nitric peroxide (NO_4).

If the experiment be made in a graduated eudiometer (fig. 137), standing over water coloured with blue litmus, the latter will very soon be reddened by the acid formed, and the air will be found to diminish very considerably in volume, eventually losing its power of supporting combustion, in consequence of the removal of oxygen.

Fig. 137.

When hydrogen gas, mixed with a small quantity of nitrogen, is burnt, the water collected from it is found to have an acid taste and reaction, due to the presence of a little nitric acid, resulting from the combination of the nitrogen with the oxygen of the air under the influence of the intense heat of the hydrogen flame.

Since all the compounds of nitrogen and oxygen are obtained, in practice, from hydrated nitric acid ($HO . NO_5$), the chemical history of that substance must precede that of the bodies enumerated in the above table.

Nitric Acid.

93. This most important acid is obtained from saltpetre, which is found as an incrustation upon the surface of the soil in hot and dry climates, as in some parts of India and Peru. The salt imported into this country from Bengal and Oude consists of nitrate of potash ($KO . NO_5$), whilst the Peruvian or Chilian saltpetre is nitrate of soda ($NaO . NO_5$). Either of these will serve for the preparation of nitric acid.

Fig. 138.—Preparation of nitric acid.

On the small scale, in the laboratory, nitric acid is prepared by distilling *nitrate of potash with an equal weight of* concentrated sulphuric acid.

In order to make the experiment, four ounces of powdered nitre, thoroughly dried, may be introduced into a pint-stoppered retort (fig. 138), and two and a half measured ounces of concentrated sulphuric acid poured upon it. As soon as the acid has soaked into the nitre, a gradually increasing heat may be applied by means of an Argand burner, when the acid will distil over. It must be preserved in a stoppered bottle.

When the acid has ceased distilling, the retort should be allowed to cool, and filled with water. On applying a moderate heat for some time, the saline residue will be dissolved. The solution may then be poured into an evaporating dish, and evaporated down to a small bulk. On allowing the concentrated solution to cool, crystals of bisulphate of potash ($KO . HO . 2SO_3$) are deposited, a salt which is very useful in many metallurgic and analytical operations.

The decomposition of nitrate of potash by an equal weight of concentrated sulphuric acid is explained by the equation—

$$\underset{\text{Nitrate of potash.}}{KO . NO_5} + \underset{\text{Hydrated sulphuric acid.}}{2(HO . SO_3)} = \underset{\text{Hydrated nitric acid.}}{HO . NO_5} + \underset{\text{Bisulphate of potash.}}{KO . SO_3, HO . SO_3}$$

It would appear at first sight that one-half of the sulphuric acid might be dispensed with, but it is found that when one equivalent only of sulphuric acid is employed, so high a temperature is required to effect the complete decomposition of the saltpetre (the above equation then representing only the first stage of the action), that much of the nitric acid is decomposed; and the neutral sulphate of potash ($KO . SO_3$), which would be the final result, is not nearly so easily dissolved out of the retort by water as the bisulphate.

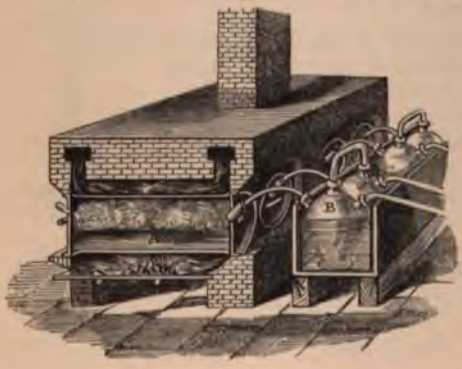


Fig. 139.—Preparation of nitric acid.

For the preparation of large quantities of nitric acid, the nitrate of soda is substituted for nitrate of potash, being much cheaper, and furnishing a larger proportion of nitric acid.

The nitrate of soda is introduced into an iron cylinder (A, fig. 139), lined with fireclay to protect it from the action of the acid, and half its weight of sulphuric acid (oil of vitriol) is poured upon it. Heat is then applied by a furnace, into which the cylinders are built, in pairs, when the hydrated nitric acid passes off in vapour, and is condensed in a series of stoneware bottles (B) surrounded with cold water.

$$\underset{\text{Nitrate of soda.}}{NaO . NO_5} + \underset{\text{Oil of vitriol.}}{HO . SO_3} = \underset{\text{Sulphate of soda.}}{NaO . SO_3} + \underset{\text{Hydrated nitric acid.}}{HO . NO_5}$$

The sulphate of soda left in the retort is useful in the manufacture of glass.

In the preparation of nitric acid, it will be observed at the beginning and towards the end of the operation, that the retort becomes filled with a red vapour. This is due to the decomposition of a portion of the colourless vapour of nitric acid by heat into water, oxygen, and nitric peroxide—

$$HO . NO_5 = HO + O + NO_4$$

this last forming the red vapour, a portion of which is absorbed by the hydrated nitric acid, and gives it a yellow colour. The pure nitric acid is colourless, but if exposed to sunlight it becomes yellow, a portion suffering this decomposition. In consequence of the accumulation of the oxygen in the upper part of the bottle, the stopper is often forced out suddenly when the bottle is opened, and care must be taken that drops of this very corrosive acid be not spirted into the face.

The strongest nitric acid (obtained by distilling perfectly dry nitre with an equal weight of pure oil of vitriol, and collecting the middle portion of the acid separately from the first and last portions, which are somewhat weaker) emits very thick grey fumes when exposed to damp air, because its vapour, though itself transparent, absorbs water very readily from the air, and condenses into very minute drops of diluted nitric acid which compose the fumes. The weaker acids commonly sold in the shops do not fume so strongly. An exact criterion of the strength of any sample of the acid is afforded by the specific gravity, which may be ascertained by the methods described at page 115, using a hydrometer adapted for liquids heavier than water. Thus, the strongest acid ($HO . NO_5$) has the specific gravity 1·52, and contains 85·72 per cent., by weight, of NO_5;* whilst the ordinary *aquafortis* or diluted nitric acid has the sp. gr. 1·29, and contains only 40 per cent. of NO_5. The concentrated nitric acid usually sold by the operative chemist (*double aquafortis*) has the sp. gr. 1·42, and contains 58 per cent. of NO_5.

A very characteristic property of nitric acid is that of staining the skin yellow. It produces the same effect upon most animal and vegetable matters, especially if they contain nitrogen. The application of this in dyeing silk of a fast yellow colour may be seen by dipping a skein of white silk in a warm mixture of concentrated nitric acid with an equal volume of water, and afterwards immersing it in dilute ammonia, which will convert the yellow colour into a brilliant orange. When sulphuric or hydrochloric acid is spilt upon the clothes, a red stain is produced, and a little ammonia restores the original colour; but nitric acid stains are yellow, and ammonia intensifies instead of removing them, though it prevents the cloth from being eaten into holes.

Nitric acid changes most organic colouring matters to yellow, but, unless very concentrated, it merely reddens litmus. If solutions of indigo and litmus are warmed in separate flasks, and a little nitric acid added to each, the indigo will become yellow and the litmus red. Here the indigo ($C_{16}H_5NO_2$) acquires oxygen from the nitric acid, and is converted into *isatine* ($C_{16}H_5NO_4$).

When hydrated nitric acid is heated, it begins to boil at 184° F., but it cannot be distilled unchanged, for a considerable quantity is decomposed into nitric peroxide, oxygen, and water, the two first passing off in the gaseous form, whilst the water remains in the retort with the nitric acid, which thus becomes gradually more and more diluted, until it contains 68 per cent. of $HO . NO_5$, when it passes over unchanged at the temperature of 248° F. The specific gravity of this acid is 1·42. If an acid weaker than this be submitted to distillation, water will pass off until acid of this strength is obtained, when it distils over unchanged.

The facility with which hydrated nitric acid parts with a portion of its

* It is extremely difficult to obtain the $HO . NO_5$ free from any extraneous water, as it undergoes decomposition *not only when vaporised* at the boiling point, but even at ordinary *temperatures*.

oxygen, renders it very valuable as an *oxidising agent*. Comparatively few substances which are capable of forming compounds with oxygen can escape oxidation when treated with nitric acid.

A small piece of phosphorus dropped into a porcelain dish containing the strongest nitric acid (and placed at some distance to avoid danger), soon begins to act upon the acid, generally with such violence as to burst out into flame, and sometimes to shatter the dish; the result of this action is hydrated phosphoric acid, the same compound which is formed in the anhydrous state, when phosphorus is burnt in oxygen gas.

When sulphur is heated with nitric acid, it is actually oxidised to a greater extent than when burnt in pure oxygen, for in this case it is converted into sulphurous acid (SO_2), whilst nitric acid imparts to it three equivalents of oxygen, forming sulphuric acid (SO_3).

Charcoal, which is so unalterable by most chemical agents at the ordinary temperature, is oxidised by nitric acid. If a mixture of the strongest nitric acid with half its volume of fuming (Nordhausen) sulphuric acid be poured upon finely powdered charcoal, the latter takes fire at once. A stick of charcoal dipped into this mixture will take fire after a few seconds.

Even iodine, which is not oxidised by free oxygen, is converted into iodic acid (IO_5) by nitric acid.

It not unfrequently happens in this manner that oxygen, in a state of unstable combination, is more prone to unite with other substances than when it is in a free state. It would seem that the disposition to combination having been once impressed upon it is retained, so as to facilitate its union with other bodies.

But it is especially in the case of metals that the oxidising powers of nitric acid are called into useful application.

Acids are not capable of uniting with metals, but only with their oxides. Hence, when a metal is dissolved by any oxygen-acid, the latter must first convert the metal into an oxide, which then combines with the acid to form a salt.

If a little black oxide of copper be heated in a test-tube with nitric acid, it dissolves, without evolution of gas, yielding a blue solution, which contains the nitrate of copper, or, to speak correctly, the nitrate of oxide of copper. In this case the oxide of copper has simply displaced the water of the hydrated acid—

$$\underset{\text{Oxide of copper.}}{CuO} + HO.NO_5 = HO + \underset{\text{Nitrate of copper.}}{CuO.NO_5}$$

But when nitric acid is poured upon metallic copper (copper turnings), a very violent action ensues, red fumes are abundantly evolved, and the metal dissolves in the form of nitrate of copper—

$$4(HO.NO_5) + Cu_3 = \underset{\text{Nitrate of copper.}}{3(CuO.NO_5)} + 4HO + \underset{\text{Nitric oxide.}}{NO_2}$$

The nitric oxide itself is colourless, but as soon as it comes into contact with the oxygen of the air, it is converted into the red nitric peroxide—

$$NO_2 + O_2 = NO_4$$

All the metals in common use are acted upon by nitric acid, except gold and platinum, so that this acid is employed to distinguish and separate these metals from others of less value. The ordinary ready *method of* ascertaining whether a trinket is made of gold consists in

touching it with a glass stopper wetted with nitric acid, which leaves gold untouched, but colours base alloys blue, from the formation of nitrate of copper. The *touch-stone* allows this mode of testing to be applied with greater accuracy. It consists of a species of black basalt, obtained chiefly from Silesia. If a piece of gold be drawn across its surface a golden streak is left, which is not affected by moistening with nitric acid; whilst the streak left by brass, or any similar base alloy, would be rapidly dissolved by the acid. Experience enables an operator to determine by means of the touch-stone pretty nearly the amount of gold present in the alloy, comparison being made with the streaks left by alloys of known composition.

Though all the metals in common use, except gold and platinum, are *oxidised* by nitric acid, they are not all *dissolved*; there are two metals, tin and antimony, which are left by the acid in the state of insoluble oxides, which possess acid properties, and do not unite with the nitric acid.

If some concentrated nitric acid be poured upon tin filings, no action will be observed;* but on adding a little water, red fumes will be evolved in abundance, and the tin will be converted into a white powder, which is the binoxide of tin (SnO_2), *putty powder*. The gas which is evolved in this case is the nitric peroxide (NO_4), and the action of the acid is represented by the equation which follows:—

$$2(HO.NO_5) + Sn = SnO_2 + 2HO + 2NO_4$$

If the white mixture of binoxide of tin with nitric acid be made into a paste with slaked lime, the smell of ammonia will be exhaled; and experiments with other metals have shown it to be a general principle, that when any metal capable of decomposing water is dissolved in diluted nitric acid, ammonia is always formed, its quantity increasing with the degree of dilution of the nitric acid; of course, the ammonia combines with the excess of acid present to form nitrate of ammonia, and the lime was added in the above experiment in order to displace the ammonia from its combination, and to exhibit its odour. This conversion of nitric acid into ammonia becomes the more interesting when it is remembered that the ammonia can be reconverted into nitric acid (p. 122).

By dissolving zinc in very diluted nitric acid, a very large quantity of ammonia may be obtained. The change is easily followed if we suppose the *nascent* hydrogen (or hydrogen with the tendency to combination still remaining impressed upon it, see p. 126), produced by the action of the zinc upon the water, to act upon the nitric acid, converting its oxygen into water, and its nitrogen into ammonia, thus—$NO_5 + H_8 = 5HO + NH_3$. The exalted attractions possessed by substances in the nascent state, that is, at the instant of their passing from a state of combination, are very remarkable, and will be found to receive frequent application.†

Action of nitric acid upon organic substances.—The oxidising action of nitric acid upon some organic substances is so powerful as to be attended with inflammation; if a little of the strongest nitric acid be placed in a porcelain capsule, and a few drops of oil of turpentine be poured into it from a test-tube fixed to the end of a long stick, the turpentine takes fire with a sort of explosion. By boiling some of the strongest acid in a test-tube (fig. 140), the mouth of which is loosely

* It is a fact which has scarcely been explained in a satisfactory manner, that the concentrated nitric acid often refuses to act upon metals which are violently attacked by the diluted acid.

† When a solution of nitrate of potash is mixed with a strong solution of caustic potash, and heated with granulated zinc and clean iron filings, ammonia is abundantly disengaged, being produced from the nitric acid by the nascent hydrogen resulting from the electrolytic action.

Recent experiments have indicated the existence of substances intermediate between the nitric acid and the ammonia into which it is finally converted. One of these, named *hydroxylamine*, NH_3O_2, has been examined. It is a well-defined base, forming crystalline *salts with the acids*.

stopped with a plug of raw silk or of horse-hair, the latter may be made to take fire and burn brilliantly in the vapour of nitric acid.

In many cases the products of the action of nitric acid exhibit a most interesting relation to the substances from which they have been produced, one or more equivalents of the hydrogen of the original compound having been removed in the form of water by the oxygen of the nitric acid, whilst the spaces thus left vacant have been filled up by the nitric peroxide resulting from the deoxidation of the nitric acid, producing what is termed a *nitro-substitution* compound. A very simple example of this displacement of H by NO_4 is afforded by the action of nitric acid upon benzole. A little concentrated nitric acid is placed in a flask, and benzole cautiously dropped into it; a violent action ensues, and the acid becomes of a deep red colour; if the contents of the flask be now poured into a large vessel of water, a heavy yellow oily liquid is separated, having a powerful odour like that of bitter almond oil. This substance, which is used to a considerable extent in perfumery under the name of essence of mirbane, is called *nitro-benzole*, and its formula, $C_{12}H_5(NO_4)$, at once exhibits its relation to benzole, $C_{12}H_6$.*

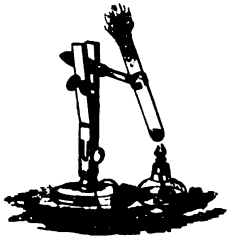


Fig. 140.

But the change does not stop here, for by continuing the action of the acid, *dinitro-benzole* $C_{12}H_4 2(NO_4)$ is obtained, in which two equivalents of hydrogen have been displaced by nitric peroxide.

It is by an action of this description that nitric acid gives rise to gun-cotton, and other explosive substances of the same class, when acting upon the different varieties of woody fibre, as cotton, paper, sawdust, &c.

The preparation and composition of gun-cotton will be described hereafter.

94. The oxidising effects of nitric acid are not confined to the free acid, but are shared to some extent by the nitrates. A mixture of nitrate of lead with charcoal explodes when sharply struck, from the sudden evolution of carbonic acid produced by the oxidation of the carbon. If a few crystals of nitrate of copper be sprinkled with water and quickly wrapped up in tin-foil, the latter will, after a time, be so violently oxidised as to emit brilliant sparks.

But in the case of bases which retain the nitric acid with greater force, such as the alkalies, the oxidation takes place only at a high temperature. If a little nitre be fused in an earthen crucible or an iron ladle, and, when it is at a red heat, some powdered charcoal, and afterwards some flowers of sulphur, be thrown into it, the energy of the combustion will testify to the violence of the oxidation. In this manner the carbon is converted into carbonate of potash ($KO.CO_2$), and the sulphur into sulphate of potash ($KO.SO_3$). See *Gunpowder*.

Combining weight of nitric acid.—Experiment proves that 47 parts by weight (1 equivalent) of potash are neutralised by 63 parts of hydrated nitric acid, and this quantity of the acid is found to contain 1 part of hydrogen, 14 parts of nitrogen, and 48 parts (6 equivalents) of oxygen. Hence the formula of the acid might be written $H.NO_6$; but if it be

* $C_{12}H_6 + HO.NO_5 = C_{12}H_5(NO_4) + 2HO.$
$C_{12}H_6 + 2(HO.NO_5) = C_{12}H_4 2(NO_4) + 4HO.$

desired to represent in the formula the mode in which the elements are grouped, the acid may be represented as composed of water combined with the anhydrous nitric acid ($HO . NO_5$).

The *unitary* (*molecular*) *formula* of nitric acid is commonly written $HN\Theta_3$ ($\Theta = 16$).

Nitrates.—Its attraction for bases places nitric acid among the strongest of the acids, though the disposition of its elements to assume the gaseous state at high temperatures, conjoined with the feeble attraction existing between nitrogen and oxygen, causes its salts to be decomposed, without exception, by heat.

The nature of the decomposition varies with the base contained in the nitrate. The nitrates of very powerful bases (such as the alkalies) are first converted into nitrites by the action of heat; thus $KO . NO_5$ gives $KO . NO_3$ and O_2; the nitrites themselves being eventually decomposed, evolving nitrogen and oxygen, and leaving the uncombined base. The nitrates of feebler bases (such as oxide of copper and oxide of lead) evolve nitric peroxide (NO_4) and oxygen, the base being left, unless it be decomposible by heat, as is the case with the oxides of silver and mercury, when the metal itself will be separated. As a general rule, the nitrates are easily soluble in water.

Comparatively few of the nitrates are in common use; the following table contains those most frequently used :—

Chemical Name.	Common Name.	Equivalent Formula.	Atomic Unitary Formula.
Nitrate of potash	Nitre, saltpetre	$KO . NO_5$	$KN\Theta_3$
Nitrate of soda	Cubic nitre, Peruvian saltpetre	$NaO . NO_5$	$NaN\Theta_3$
Nitrate of strontia	Nitrate of strontian	$SrO . NO_5$	$SrN\Theta_3$
Basic nitrate of bismuth	Trisnitrate of bismuth, Flake white	$BiO_3 . NO_5 . HO$	$2BiN\Theta_4 . H_2\Theta$
Nitrate of silver	Lunar caustic	$AgO . NO_5$	$AgN\Theta_3$

95. *Anhydrous nitric acid* or *nitric anhydride* is obtained by gently heating nitrate of silver in a slow current of chlorine, great care being taken to exclude every trace of water—

$$AgO . NO_5 + Cl = \underset{\text{Chloride of silver.}}{AgCl} + O + \underset{\text{Nitric anhydride.}}{NO_5}$$

The anhydride is condensed as a crystalline solid in a receiver cooled with ice and salt. It forms transparent colourless prisms which liquefy at 85° F., and boil at 113°. By a slightly higher temperature it is readily decomposed; and it has been said to decompose, even at the ordinary temperature, in sealed tubes which were shattered by the evolved gas.

When the anhydride is brought in contact with water, much heat is evolved, and hydrated nitric acid is produced.

The discovery of the anhydrous nitric acid by Deville in 1848, was welcomed by many chemists as a confirmation of that view of the constitution of nitric acid which had been generally received for thirty years, and which represented the acid as a compound of water with NO_5. The more modern speculative views, however, discard this substance as the true radical of nitric acid and the nitrates, and represent the *latter by formulæ which disown all connexion* with the anhydride. Thus, the mole-

cular formula for the anhydride would be written $N_2\Theta_5$, and its action upon water would be $N_2\Theta_5 + H_2\Theta = 2HN\Theta_3$.

96. *Nitrous oxide* or *laughing gas* is prepared by heating nitrate of ammonia, when it is resolved into water, and nitrous oxide*—

$$NH_3.HO.NO_5 = 4HO + 2NO.$$

Nitrate of ammonia is obtained by adding fragments of carbonate of ammonia to nitric acid† diluted with an equal volume of water, until the carbonate no longer effervesces in the liquid, which is then evaporated down until a drop solidifies on a cold surface, when the whole may be poured out upon a clean stone, and the mass broken up and preserved in a well-stoppered bottle, because it is liable to attract moisture from the air. To obtain the nitrous oxide, an ounce of the salt may be gently heated in a small retort, when it melts, boils, and gradually disappears entirely in the forms of steam and nitrous oxide. The latter may be collected with slight loss over water.

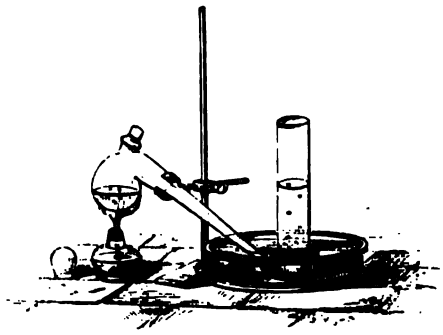


Fig. 141.

Nitrous oxide is perfectly colourless, but has a slight odour and a sweetish taste. Its characteristic intoxicating property is well known. It accelerates the combustion of a taper like oxygen itself, and will even kindle into flame a spark at the end of a match. It can readily be distinguished from oxygen, however, by shaking it with water, which absorbs, at the ordinary temperature, about three-fourths of its volume of the nitrous oxide. It is also much heavier than oxygen, its specific gravity being 1·53, and is not a permanent gas, being liquefied by a pressure of 40 atmospheres at 45° F., and solidified at −150° F. The liquid nitrous oxide possesses a special interest, for, by mixing it with bisulphide of carbon, and evaporating *in vacuo*, the lowest temperature hitherto known has been obtained, viz., −220° F.

97. *Nitric oxide* or *binoxide of nitrogen* is usually obtained by the action of copper upon diluted nitric acid—

$$4(HO.NO_5) + Cu_3 = 3(CuO.NO_5) + NO_2 + 4HO.$$

300 grains of copper turnings or clippings are introduced into a retort, and three measured ounces of a mixture of concentrated nitric acid with an equal volume of water are poured upon them. A very gentle heat may be applied to assist the action, and the gas may be collected over water (see fig. 141), which absorbs the red fumes (NO_4) formed by the union of the NO_2 with the air contained in the retort.

Nitric oxide is distinguished from all other gases by the production of a red gas, when the colourless nitric oxide is allowed to come in contact with uncombined oxygen, the presence of which, in mixtures of gases, may be readily detected by adding a little nitric oxide. The red gas consists

* By passing the mixture of nitrous oxide and aqueous vapour over hydrate of potash at a dull red heat, nitric acid and ammonia are reproduced.

† Which must remain clear when tested with nitrate of silver, showing it to be free from chlorine.

chiefly of nitric peroxide (NO_4), but it often contains also some (NO_3) nitrous acid.

The combination of nitric oxide with oxygen may be exhibited by decanting a pint bottle of oxygen, under water, into a tall jar filled with water coloured with blue litmus, and adding to it a pint bottle of nitric oxide (fig. 142). Strong red fumes are immediately produced, and on gently agitating the cylinder, the fumes are absorbed by the water, reddening the litmus. The oxygen will now have been reduced to half its volume, and if another pint of nitric oxide be added, the remainder of the oxygen will be absorbed, showing that *two volumes of nitric oxide combine with one volume of oxygen*, forming the nitric peroxide which is absorbed by the water.

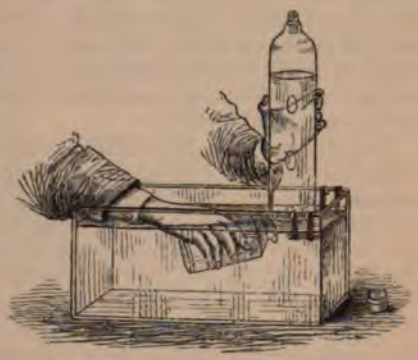


Fig. 142.

The addition of nitric oxide to atmospheric air was one of the earliest methods employed for removing the oxygen in order to determine the composition of air; but important variations were observed in the results, in consequence of the occasional formation of NO_3 in addition to the NO_4.

The rough analysis of air by this method may be instructively performed with two similar gas cylinders, each divided into ten equal volumes. Into one are introduced five volumes of air, and into the other five volumes of nitric oxide. On decanting the air, under water, into the nitric oxide (fig. 143), the red nitric peroxide will be formed and absorbed by the water, the ten volumes of gas shrinking to seven, showing that three volumes have been absorbed, of which one volume would of course represent the oxygen contained in the five volumes of air.

The nitric oxide prepared by the action of copper on nitric acid generally contains nitrous oxide, and will seldom give correct results in the above experiment. Pure nitric oxide may be obtained by heating in a retort 100 grains of nitrate of potash, 1000 grains of sulphate of iron, and three measured ounces of diluted sulphuric acid (containing one measure of acid to three measures of water), which will yield above two pints of the gas.*

Fig. 143.

In all its properties, nitric oxide is very different from nitrous oxide. It is much lighter, having almost exactly the same specific gravity as air, viz., 1·04, has never yet been liquefied, and is not dissolved to any important extent by water. When a lighted taper is immersed in nitric oxide, it is extinguished, although this gas contains twice as much oxygen as nitrous oxide, which so much accelerates the combustion of a taper, for the elements are held together by a stronger attraction in the nitric oxide, so that its oxygen is not so readily available for the support of combustion. (The nitric oxide prepared from copper and nitric acid sometimes contains so much nitrous oxide that a taper burns in it brilliantly.)

* $KO.NO_5 + 6(FeO.SO_3) + 4(HO.SO_3) = KO.SO_3 + 3(Fe_2O_3.3SO_3) + NO_4 + 4HO.$

Even phosphorus, when just kindled, is extinguished in nit but when allowed to attain to full combustion in air, it b extreme brilliancy in the gas. Indeed, nitric oxide appears to b easy of decomposition of the whole series of oxides of nitro accounts for its being the most common result of the decom the other oxides. Nitrous oxide itself, when passed through tube, is partly converted into nitric oxide; and when a taper bottle of nitrous oxide, the upper part of the bottle is often fil red gas, indicating the formation of nitric oxide, and its oxidat air entering the bottle.

The difference in the stability of the two gases is also show behaviour with hydrogen. A mixture of nitrous oxide with volume of hydrogen explodes when in contact with flame, yiel and nitrogen, but a mixture of equal volumes of nitric oxide a gen burns quietly in air, the hydrogen not decomposing the ni An excess of hydrogen, however, is capable of decomposing ni ammonia and water being formed.

If two volumes of nitric oxide be mixed with five volumes of hydrog gas passed through a tube having a bulb filled with platinised asbestos the mixture issuing from of the tube will produce pours by contact with the will strongly redden blue if the platinised asbestos with a spirit-lamp, the hy couraged by the action o num (91) will decompose oxide, and strongly alkal of ammonia will be prod ing the blue colour to t litmus: $NO_2 + H_6 = N$ It will be remembered oxygen is in excess, amm verted, under the influen num, into water and nitro

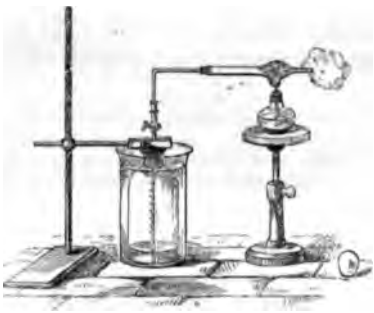


Fig. 144.

Nitric oxide is readil by ferrous salts (salts of of iron) with which it forms dark brown solutions. If a little sulphate of iron be shaken in a cylinder of nitric oxide closed w plate, the gas will be immediately absorbed, and the solution w dark brown. On applying heat, the brown compound is de A compound of 4 eqs. of ferrous sulphate and 1 eq. of nitric been obtained in small brown crystals, which lose all their n *in vacuo*.

98. *Nitrous acid.*—This acid is said to exist, as nitrite of an minute quantity, in rain water, and is occasionally found in co with alkalies or alkaline earths, in well-waters, where it has pro formed by the oxidation of ammonia (91). Small quantities of ammonia appear to be formed by the combustion in air of gas ing hydrogen, this element uniting with the atmospheric ox nitrogen.

Nitrous acid may be obtained by heating starch with nitri the most convenient process consists in gently heating nitric

* *Asbestos* which has been wetted with solution of bichloride of platinum *heated to redness*, to reduce the platinum to the metallic state.

gr. 1·35) with an equal weight of arsenious acid, and passing the gas, first through a U-tube (fig. 145) surrounded with cold water, to condense un-

Fig. 145.—Preparation of nitrous acid.

decomposed nitric acid, then through a similar tube containing chloride of calcium, to absorb aqueous vapour, and afterwards into a U-tube surrounded with a freezing mixture of ice and salt. Through a small tube opening into the bend of this U-tube, the condensed nitrous acid drops into a tube drawn out to a narrow neck, so that it may be drawn off, and sealed by the blowpipe.

$$HO.NO_5 + \underset{\text{Arsenious acid.}}{AsO_3} = \underset{\text{Arsenic acid.}}{HO.AsO_5} + NO_4.$$

The nitrous acid is thus obtained as a blue liquid which boils below 32° F., becoming converted into a red vapour. Water at about 32° F. dissolves the acid without decomposing it, yielding a blue solution which is decomposed, as the temperature rises, into nitric acid which remains in the liquid, and nitric oxide which escapes with effervescence—

$$3NO_3 + HO = HO.NO_5 + 2NO_2.$$

The salts of nitrous acid, or *nitrites*, are interesting on account of their production from the nitrates by the action of heat (p. 129).

If nitrate of potash be fused in a fire-clay crucible and heated to redness, it will evolve bubbles of oxygen, and slowly become converted into nitrite of potash ($KO.NO_3$). The heat should be continued until a portion removed on the end of an iron rod, and dissolved in water, gives a strongly alkaline solution. The fused mass may then be poured upon a *dry* stone, and when cool, broken into fragments and preserved in a stoppered bottle. On heating a fragment of the nitrite of potash with diluted sulphuric acid, red vapours will be disengaged, but these contain but little nitrous acid, the greater part of which is decomposed by the water into nitric acid and nitric oxide.

When nitrous acid acts upon ammonia, both compounds suffer decomposition, water and nitrogen being the results—

$$NH_3 + NO_3 = N_2 + 3HO.$$

This is sometimes taken advantage of in preparing nitrogen gas by boiling mixed solutions of sal-ammoniac and nitrite of potash—

$$\underset{\text{Sal-ammoniac.}}{NH_3.HCl} + KO.NO_3 = N_2 + KCl + 4HO.$$

In experiments upon organic compounds, nitrous acid is sometimes employed as a convenient agent for effecting simultaneously the removal of three equivalents of hydrogen from a compound, and the insertion of one equivalent of nitrogen.

When solutions of nitrites are heated in contact with air, they gradually absorb *oxygen, becoming converted into nitrates.*

99. *Nitric peroxide*, also called *hyponitric acid* and *peroxide of nitrogen* or *pernitric oxide:* formerly known as *nitrous acid.*—By passing a mixture of nitric oxide with half its volume of oxygen, free from every trace of moisture, into a perfectly dry tube cooled in a mixture of ice and salt, the dark red gas is condensed into colourless prismatic crystals, which melt at 10° F. into a nearly colourless liquid. This gradually becomes yellow as the temperature rises, and at the ordinary temperature has a deep orange colour. It is very volatile, boiling at 71° F., and being converted into a red-brown vapour, which was long mistaken for a permanent gas, on account of the great difficulty of condensing it when once mixed with air or oxygen. Nitric peroxide is also obtained, mixed with one-fourth of its volume of oxygen, by heating the nitrate of lead (fig. 146)—

$$PbO.NO_5 = PbO + NO_4 + O.$$

The vapour of nitric peroxide is much heavier than atmospheric air. Its colour varies with the temperature, becoming very dark at 100° F. The smell of the vapour is very characteristic. It supports the combustion of strongly burning charcoal or phosphorus, and oxidises most of the metals, potassium taking fire in it spontaneously. The nitric peroxide must, therefore, rank as a powerful oxidising agent, and it is the presence of this substance in the red fuming nitric acid that imparts to it higher oxidising powers than those of the colourless nitric acid.

Fig. 146.—Preparation of nitric peroxide.

The so-called *nitrous acid* of commerce is really nitric acid holding in solution a large proportion of nitric peroxide, and is prepared by introducing sulphur into the retorts containing the mixture of nitrate of soda and sulphuric acid employed in the preparation of the nitric acid, a portion of which is deoxidised and converted into nitric peroxide. Water immediately decomposes the nitric peroxide into nitric oxide and nitric acid—

$$3NO_4 + 2HO = NO_2 + 2(HO.NO_5).$$

When water is gradually added to liquid nitric peroxide, it effervesces, from escape of nitric oxide, and becomes green, blue, and ultimately colourless. The production of the green and blue colours appears to be due to the solution of the unaltered NO_4 in the nitric acid produced, and when this is decomposed by an excess of water, the liquid, of course, becomes colourless. If the red nitric acid of commerce be gradually diluted with water, it will be found to undergo similar changes, always becoming colourless at last. The nitric acid which has been used in a Grove's battery always has a green colour from the large amount of nitric peroxide which has accumulated in it during the action of the battery, in consequence of the decomposition of the acid by the hydrogen disengaged during the action of the battery; $H + HO.NO_5 = 2HO + NO_4$. If this green acid be diluted with a little water, it becomes blue, and a larger quantity of water renders it colourless, causing the evolution of nitric oxide. Similar colours are obtained by passing nitric oxide into nitric acid of different degrees of concentration, apparently because nitric peroxide is formed and dissolved by the acid—

$$NO_2 + 2(HO.NO_5) = 3NO_4 + 2HO.$$

When silver, mercury, and some other metals are dissolved in cold nitric

d, a green or blue colour is often produced, leading a novice to suspect e presence of copper, the colour being really caused by the solution in e unaltered nitric acid of the nitric peroxide produced by the deoxida- n of another portion.

Nitric peroxide was formerly believed to be an independent acid capable forming salts. It is true that its vapours have a strongly acid reaction test-papers, but when brought into contact with bases, it produces a xture of nitrate and nitrite—

$$NO_4 + 2(KO.HO) = KO.NO_5 + KO.NO_3 + 2HO.$$

100. *General review of the oxides of nitrogen.*—All the above oxides of trogen are directly obtainable from nitric acid by the action of metals; t since the result of such action varies much with the temperature and te of concentration of the acid, it cannot be depended upon for the eparation of the oxides in a separate state.

Nitric peroxide is the chief product of the action of tin upon nitric acid—

$$2(HO.NO_5) + Sn = 2HO + 2NO_4 + SnO_2.$$

itrous acid is abundantly formed when silver is acted on by nitric acid—

$$3(HO.NO_5) + Ag_2 = 3HO + NO_3 + 2(AgO.NO_5).$$

itric oxide has been shown to be evolved when nitric acid is deoxidised copper—

$$4(HO.NO_5) + Cu_4 = 4HO + NO_2 + 3(CuO.NO_5);$$

ough, if the acid be concentrated or the temperature high, nitrous oxide d nitrogen are mixed with the nitric oxide.

Nitrous oxide is given off when zinc is dissolved in nitric acid diluted th ten measures of water—

$$5(HO.NO_5) + Zn_4 = 5HO + NO + 4(ZnO.NO_5);$$

e nitrous oxide, however, is mixed with nitric oxide.

Nitric oxide, nitrous acid, and nitric peroxide, are very remarkable for eir relations to oxygen. Nitric oxide is one of the very few substances ich combine with dry oxygen at the ordinary temperature, and yet the tric peroxide which is thus produced is very ready to yield its oxygen other substances. Nitrous acid, as might be expected, is intermediate this respect, being capable of acting as a reducing agent upon power- lly oxidising substances, and as an oxidising agent upon substances ving a great attraction for oxygen. Thus, a solution of nitrite of tash, acidified with sulphuric acid, will bleach permanganate of potash, lucing the permanganic acid (Mn_2O_7) to manganous oxide (MnO); ilst, if added to sulphate of iron, the nitrite converts the ferrous oxide eO) into ferric oxide (Fe_2O_3), and this solution, which was capable of lucing the permanganate of potash before, is now found to be without ect upon it, unless an excess of the nitrite has been added.

The oxides of nitrogen, as illustrating combination in multiple propor- ns by weight and volume.—In its most general form, the *law of multiple oportions* may be thus stated. When a substance (A) combines with other substance (B) in more than one proportion, the quantities of B, ich combine with *a constant quantity* of A, are multiples of the smallest mbining quantity of B by some whole number.

In the oxides of nitrogen this law is exemplified in the simplest form, *ce the quantities of oxygen which combine* with a constant quantity of

nitrogen, are multiples of the least combining quantity of oxygen by 2, 3, 4, and 5 (see table, p. 123).

It was shown, at p. 120, that there is ground for representing the combining weight of nitrogen as = 14, and its combining volume as = 2 (the combining volume of oxygen being = 1).

When nitrous oxide is passed through a red-hot porcelain tube, its volume is increased by one-half, and the resulting gas is found to be a mixture of one volume of oxygen and two volumes of nitrogen. Hence it is inferred that, in nitrous oxide, two volumes (representing one combining weight, or 14 parts) of nitrogen are united with one volume (representing one combining weight, or 8 parts) of oxygen, to form two volumes of nitrous oxide (representing 22 parts by weight). But whether this quantity represents one equivalent, or more than one equivalent, of nitrous oxide, cannot be determined by experiment, because this oxide is not known to enter into any sufficiently definite combination with other substances. If the equivalent of nitric acid (NO_5) be represented by 54, as deduced from the experiment cited at p. 128, it would appear most convenient to assume the equivalent of nitrous oxide as = 22, since that quantity results from the deoxidation of one equivalent of nitric acid.

When charcoal is strongly heated in nitric oxide, the volume of the gas remains unchanged; but it is found, on analysis, to have become converted into a mixture of equal volumes of carbonic acid and nitrogen ($NO_2 + C = CO_2 + N$). Since one volume of carbonic acid contains one volume of oxygen (page 80), the experiment proves that one volume of oxygen and one volume of nitrogen exist in two volumes of nitric oxide, or that two volumes of nitrogen (representing one combining weight, or 14 parts) are combined with two volumes of oxygen (representing two combining weights, or 16 parts) in four volumes (representing 30 parts by weight) of nitric oxide. The circumstance that this quantity of nitric oxide is capable of forming a definite compound with one equivalent of chlorine, and that it is the quantity resulting from the decomposition of one equivalent of nitric acid, appears to justify the conclusion that the equivalent of nitric oxide is represented by NO_2 = 30 parts by weight = 4 volumes.

The direct evidence of the composition of nitrous acid is not so satisfactory as that in the two preceding cases. This acid has been obtained, however, by the direct union of one volume of oxygen with four volumes of nitric oxide, leading to the conclusion that it contains NO_3. Its equivalent has been determined by the analysis of nitrite of silver, which was found to contain, for one equivalent (116 parts by weight) of oxide of silver, 38 parts by weight of nitrous acid, representing a compound of 14 parts by weight of nitrogen (or one equivalent = 2 volumes), with 24 parts by weight (or three equivalents = 3 volumes) of oxygen. The volume occupied by the equivalent of nitrous acid in the state of vapour has not yet been ascertained, no accurate determination of the specific gravity of its vapour having been made.

Nitric peroxide has been analysed by passing the vapour produced from a known weight of the liquid over red-hot metallic copper, which absorbed the oxygen, leaving the nitrogen to be collected and measured. It was thus found that 14 parts by weight (one equivalent = 2 volumes) of nitrogen were combined with 32 parts by weight (four equivalents = 4 volumes) of oxygen, a result which is confirmed by the direct union of 4 volumes of NO_2 (one equivalent) with 2 volumes of oxygen (two equivalents) to form NO_4.

The circumstance that 46 parts by weight of nitric peroxide are capable of displacing one equivalent of hydrogen in organic substances (page 128), supports the belief that the formula NO_4 (= 46 by weight) represents the equivalent of nitric peroxide. The results of experiments upon the specific gravity of its vapour have been so unsatisfactory, on account of its variation at different temperatures, that the volume occupied by an equivalent of nitric peroxide can scarcely be said to be satisfactorily established. It is, however, generally believed to represent four volumes (containing 2 volumes of nitrogen and 4 volumes of oxygen).

Nitric anhydride, or anhydrous nitric acid, was analysed by a method similar to that employed for nitric peroxide, and was found to contain 14 parts by weight (one equivalent = 2 volumes) of nitrogen, combined with 40 parts (five equivalents = 5 volumes) of oxygen, forming 54 parts of nitric anhydride, the quantity which is united with one equivalent (47 parts) of potash in nitrate of potash, and which may *therefore be taken* to represent the equivalent of the anhydride. The volume occu-

y the equivalent of nitric anhydride in the state of vapour has not been deter-
, on account of the want of stability of this compound.

e following table exhibits a general view of the composition and
alents of the oxides of nitrogen, a note of interrogation (?) being
oyed to show where the number has been deduced from hypothetical
derations instead of experimental results :—

	Equivalent Formula.	Equivalent Weight.	By Weight.		Equivalent Volume.	By Volume.	
			N	O		N	O
rous oxide,	NO	22?	14	8	2?	2	1
ric oxide,	NO_2	30	14	16	4	2	2
rous acid,	NO_3	38	14	24	4?	2	3
ric peroxide,	NO_4	46	14	32	4?	2	4
ric acid,	NO_5	54	14	40	4?	2	5

omic constitution of the oxides of nitrogen.—Assuming that one atom
elementary substance always occupies one volume, nitrous oxide
aining 2 vols. nitrogen and 1 vol. oxygen) would be represented by
atomic formula $N_2\Theta$ ($\Theta = 16$); nitric oxide (containing 1 vol.
gen and 1 vol. oxygen), would become $N\Theta$; nitrous acid (containing
s. nitrogen and three vols. oxygen) would be $N_2\Theta_3$; nitric peroxide
aining 1 vol. nitrogen and 2 vols. oxygen), $N\Theta_2$; and anhydrous
acid (containing 2 vols. nitrogen and 5 vols oxygen), $N_2\Theta_5$. These
ulæ, however, have the disadvantage of wanting that symmetrical re-
to each other which affords so great assistance in recollecting the
osition of such a series of compounds. The symmetry may be pre-
d by writing the formula of nitric oxide as a double molecule (4 vols.),
ssuming that nitrous acid, nitric peroxide, and nitric acid have really
our-density corresponding to a two-volume formula; thus—

(H = 1 vol.)
$N_2\Theta$ = 2 vols.
$N_2\Theta_2$ = 4 vols.
$N_2\Theta_3$ = 2 vols.?
$N_2\Theta_4$ = 2 vols.?
$N_2\Theta_5$ = 2 vols.?

CHLORINE.

1. This element is never found in the uncombined state, but is very
dant in the mineral world in the forms of chloride of sodium (common
and chloride of potassium. In these forms also it is an important
ituent of the fluids of the animal body, but as it is not found in
ient proportion in vegetable food, or in the solid parts of animal food,
antity of salt must be added to these in order to form a wholesome
Chloride of sodium is indispensable as a raw material for several of
nost useful arts, such as the manufactures of soap and glass, bleaching,
in fact, it is the source of three of the most generally useful chemical
ucts, viz., chlorine, hydrochloric acid, and soda.

About the middle of the seventeenth century, a German chemist named Glauber distilled some common salt with sulphuric acid, and obtained a strongly acid liquid to which he gave the name *muriatic acid* (from *muria*, *brine*) and which was proved to be identical with the acid long known to the alchemists as *spirit of salt*. The saline mass which was left after the experiment was then termed Glauber's salt, but afterwards received its present name of sulphate of soda.

It was undoubtedly a natural inference from this experiment that common salt was composed of muriatic acid and soda, and that the sulphuric acid had a greater attraction for the soda than the muriatic acid, which was therefore displaced by it. In accordance with this view, common salt was called muriate of soda, without further question until the year 1810, when the experiments of Davy proved that it was really composed of the two elementary substances, chlorine and sodium, and must therefore be styled, as it now is, chloride of sodium, and represented by the formula NaCl. It was further shown by Davy, that the muriatic acid was really composed of chlorine and hydrogen, and that it was, in fact, chloride of sodium (NaCl) in which the sodium had been displaced by hydrogen (HCl).

Preparation of chlorine.—In order to extract chlorine from common salt, it is heated with black oxide of manganese and diluted sulphuric acid; the acid decomposes the binoxide of manganese, part of the oxygen of which displaces the chlorine from the chloride of sodium, yielding soda which combines with the sulphuric acid, so that the sulphates of soda and manganese are left in solution, and chlorine escapes in the form of gas;

$$NaCl + MnO_2 + 2(HO.SO_3) = NaO.SO_3 + MnO.SO_3 + 2HO + Cl.$$

600 grains of common salt may be mixed with 450 grains of binoxide of manganese, introduced into a retort (fig. 147), and a cold mixture of 1½ oz. by measure of strong sulphuric acid with 4 oz. of water poured upon it. The retort having been well

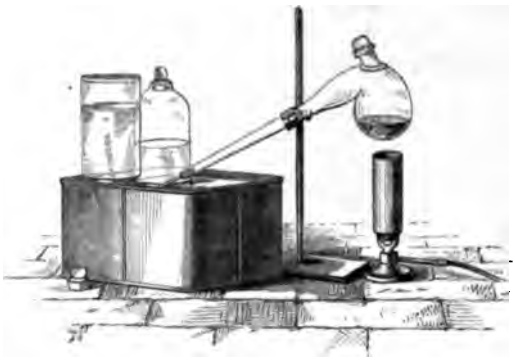


Fig. 147.—Preparation of chlorine.

shaken to wet the powder thoroughly with the acid, a very gentle heat is applied, and the gas collected in bottles filled with water and inverted in the pneumatic trough. When the bottles are filled, the stoppers, previously greased, must be inserted into them under water. The first bottle or two will contain the air from the retort, and will therefore have a paler colour than the pure chlorine afterwards collected. It is advisable to keep a jar filled with water standing ready on the shelf of the trough, so that any excess of chlorine may be passed into it instead of being allowed to escape into the air, causing serious inconvenience. The bottles of moist chlorine must always be preserved in the dark. Chlorine may also be conveniently

prepared by gently heating 500 grains of binoxide of manganese with 4 oz. (measured) of common hydrochloric acid—

$$MnO_2 + 2HCl = MnCl + 2HO + Cl.$$

Either of the above methods will furnish about five pints of chlorine.

Properties of chlorine.—The physical and chemical properties of chlorine are more striking than those of any element hitherto considered. Its colour, whence it derives its name (χλωρός, pale green) is bright greenish yellow, its odour insupportable. It is twice and a half as heavy as air (sp. gr. 2·47), and may be reduced to the liquid state by a pressure of only four atmospheres at 60° F. If a bottle of chlorine be held mouth downwards in water, its stopper removed, one-third of the chlorine decanted into a jar, and the rest of the gas shaken with the water in the bottle, the mouth of which is closed by the palm of the hand (fig. 148), the water will absorb twice its volume of chlorine, producing a vacuum in the bottle which will be held firmly against the hand by atmospheric pressure. If air be then allowed to enter, and the bottle again shaken as long as any absorption takes place, a saturated solution of chlorine (*chlorine water*) will be obtained. By exposing this yellow solution to a temperature approaching 32° F., yellow crystals of *hydrate of chlorine* (Cl + 10 HO) are obtained, the liquid becoming colourless.

Fig. 148.

When the water in the pneumatic trough, over which chlorine is being collected, happens to be very cold, the gas is often so foggy as to be quite opaque, in consequence of the deposition of minute crystals of the hydrate. On standing, the gas becomes clear, crystals of the hydrate being deposited like hoar-frost upon the sides of the bottle; the gas also becomes clear when the bottles are slightly warmed.

The hydrate of chlorine affords a convenient source of liquid chlorine. A number of bottles of saturated solution of chlorine, prepared as above, are exposed on a cold winter's day until the hydrate has crystallised. The crystals are thrown upon a filter, cooled to nearly 32°, allowed to drain, and rammed into a pretty strong tube closed at one end, about twelve inches long, and half an inch in diameter, previously cooled in ice or snow. The tube having been nearly filled with the crystals is kept surrounded with snow, whilst its upper end is gradually softened in the blowpipe flame and drawn off so as to be strongly sealed. When this tube is immersed in warm water, the chlorine separates from the water, and two layers of liquid are formed, the lower one consisting of amber-yellow liquid chlorine (sp. gr. 1·33), and the upper, about three times its volume, of a pale yellow aqueous solution of chlorine. On allowing the tube to cool again, the crystalline hydrate is reproduced, even at common temperatures, being more permanent under pressure.

Liquid chlorine may also be obtained in a state in which it can be preserved, by disengaging the chlorine in a sealed tube (as in the liquefaction of ammonia) from about 200 grains of bichloride of platinum previously dried at 400° F. The bichloride is heated with a spirit-lamp in one limb of the tube, whilst the other is immersed in a freezing mixture. The face and hands of the operator should be protected against the bursting of the tube.

The most characteristic chemical feature of chlorine is its powerful attraction for many other elements at the ordinary temperature. Among the non-metals, hydrogen, bromine, iodine, sulphur, selenium, phosphorus, and arsenic, combine spontaneously with chlorine, and nearly all the metals behave in the same way.

If a piece of dry phosphorus be placed in a deflagrating spoon, and immersed in a bottle of chlorine (*fig. 149*), *it will take fire spontaneously*, combining with the chlorine *to form terchloride of phosphorus* (PCl_3). A tall glass shade may be placed

over the bottle, which should stand in a plate containing water, so that the fumes may not escape into the air.

If phosphorus be placed in a bottle of oxygen to which a small quantity of chlorine has been added, it will burst out after a minute or two into most brilliant combustion.

Fig. 149.

Powdered antimony (the metal, not the sulphide), sprinkled into a bottle of chlorine (fig. 150), descends in a brilliant shower of white sparks, the antimony burning in the chlorine to form terchloride of antimony ($SbCl_3$). A little water should be placed at the bottom of the bottle to prevent it from being cracked, and the fumes should be restrained by a shade standing in water.

If a flask, provided with a stop-cock (fig. 151), be filled with leaves of *Dutch metal* (an alloy of copper and zinc, resembling gold leaf), exhausted of air, and screwed on to a capped jar of chlorine standing over water, it will be found, on opening the stop-cocks so that the chlorine may enter the flask, that the metal burns with a red light, forming thick yellow fumes containing chloride of copper (CuCl) and chloride

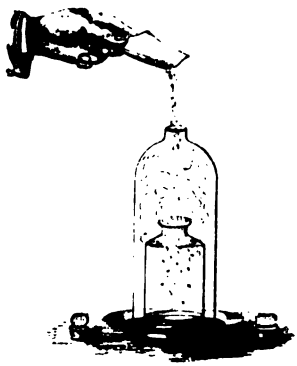


Fig. 150.

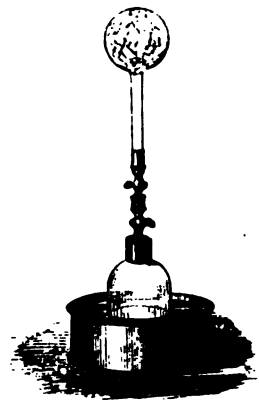


Fig. 151.

of zinc (ZnCl). If gold leaf be suspended in chlorine, it will not be immediately attacked, but will gradually become converted into terchloride of gold ($AuCl_3$).

102. The most important useful applications of chlorine depend upon its powerful chemical attraction for hydrogen. The two gases may be mixed without combining, if kept in the dark, but when the mixture is exposed to light, they combine to form hydrochloric acid gas (HCl), with a rapidity proportionate to the intensity of the *actinic* rays (or rays capable of inducing chemical change) in the light employed. Exposed to gas-light or ordinary diffused daylight, the hydrogen and chlorine combine slowly, but direct sunlight causes sudden combination, attended with explosion, resulting from the expansion which the hydrochloric acid formed suffers by the heat evolved in the act of combination. The light of magnesium burning in air, and some other artificial lights, also cause sudden com-
'nation.

"wo pint gas-bottles should be ground so that their mouths may be fitted accu-
'y to each other, and filled respectively with dry hydrogen and dry chlorine, both
having been dried by passing through oil of vitriol, and collected, the hydrogen
ward, and the chlorine by downward, displacement of air. The mouths should

slightly greased before the bottles are filled with gas, and afterwards closed with ass plates. On placing the bottles together, and removing the plates so that the ases may come in contact (see fig. 133), the yellow colour of the chlorine will be rmanent as long as the mixture is kept in the dark, but on exposure to daylight ie colour will gradually disappear, the hydrochloric acid gas being colourless. If ie bottles be now closed with glass plates, the small quantity of gas which escapes uring the operation will be seen to fume strongly in air, a property not possessed ither by hydrogen or chlorine, and when the necks of the bottles are immersed in ater and the glass plates withdrawn, the water will rapidly absorb the gas, and be rced into the bottles so as to fill them, with the exception of a small space occupied y the air accidentally admitted, showing that the hydrochloric acid gas possesses he joint volumes of the hydrogen and chlorine. If the water be tinged with blue tmus it will be strongly reddened as it enters the bottles.

The sudden union of the gases with explosion may be safely exhibited in a Flor nce flask. The flask is filled with water, which is then poured out into a measure. Exactly half the water is returned o the flask, and its level in the atter carefully marked with a dia mond or file. The flask having been gain filled with water, is closed with he thumb and inverted in the pneu matic trough, so that hydrogen may e passed up into it to displace one half of the water. A short-necked unnel is then inserted, under the vater, into the neck of the flask, nd chlorine rapidly decanted up rom a gas-bottle (fig. 152) until the est of the water has been displaced. The flask is now raised from the vater and quickly closed with a cork fig. 153), through which pass two utta-percha-covered copper wires, he ends of which have been stripped and brought sufficiently near to each other o allow of the passage of the electric spark within the flask. The ends external to the flask are also stripped and bent into hooks for convenient connexion with the conducting wires. The flask is placed upon the ground, and covered with a wooden box to prevent the pieces from flying about. On connecting the copper wires with the conducting wires from an induction-coil or an electrical machine, it will be heard, on passing the spark, that the mixture has violently exploded; on raising the box it will be found filled with strong fumes of hydrochloric acid, and a heap of small fragments of glass will represent the flask.

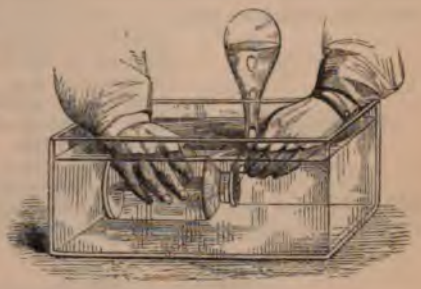


Fig. 152.

Fig. 153.

A flask filled in the same way with the mixture of hydrogen and chlorine may be attached to the end of a long stick, and thrust out into the sunlight, when it explodes with great violence.

To illustrate the direct combination of hydrogen and chlorine under the influence of artificial light, it is better to employ the mixture of exactly equal volumes of the two gases obtained by decomposing hydrochloric acid by the galvanic current. The voltameter (A, fig. 154) is filled with concentrated hydrochloric acid, and its conducting wires (B) connected with the terminals of a Grove's battery of five or six cells. Chlorine is at once evolved at the positive pole (or that connected with the platinum in the battery), and hydrogen at the negative pole (attached to the zinc of the battery). It is advisable to place the voltameter in a *vessel of cold water, to prevent the hydrochloric* acid from becoming too hot. The

gas evolved during the first five minutes should be allowed to pass into a waste-jar, because, until the liquid becomes saturated with chlorine, the evolved gas does not contain exactly equal volumes of the constituent elements. A very thin glass bulb (C), about 2 inches in diameter, blown upon a stout piece of tube, the ends of which have been drawn out to narrow open points (fig. 155), is then connected with the voltameter by means of a caoutchouc tube. A similar caoutchouc tube is attached to the free end of the bulb. When the colour of the gas in the bulb (which should be shaded from sunlight) shows that it is completely filled, the caoutchouc tubes are well closed by nipper-taps (fig. 156), and the bulb detached from the voltameter. In this condition it may be kept in the dark for a long time without alteration or escape of gas. The mixture may be most effectively exploded by exposing it to the flash of light evolved by firing a mixture of nitric oxide gas with vapour of bisulphide of carbon. For this purpose a cylinder may be filled with nitric oxide (page 130) over water, closed with a glass plate, and placed mouth upwards upon the table; the glass plate being lifted for an instant, a few drops of bisulphide of carbon are poured into the cylinder, which is then shaken. The bulb containing the explosive mixture is suspended at some distance from the operator, and the gas-cylinder is placed within a few inches of it (fig. 157). On applying a light to the cylinder, the flash will cause the immediate explosion of the mixture in the bulb, with production of strong fumes of hydrochloric acid.

Fig. 154.

Fig. 155.

Fig. 156.—Nipper-tap.

If the bulb be thin, no injury will be inflicted by the pieces of glass, or the operator may easily protect his face by a screen.

The attraction of chlorine for hydrogen enables it to effect the decomposition of water. The solution of chlorine in water may be preserved in the dark without change; but when exposed to light it loses the smell of chlorine, and becomes converted into weak hydrochloric acid, the oxygen being liberated; $HO + Cl = HCl + O$.* The decomposition takes place much more quickly at a red heat, so that oxygen is obtained in abundance by passing a mixture of chlorine and steam through a red-hot tube.

Fig. 157.

For this experiment a porcelain tube is employed, which is bound round with sheet copper to prevent it from cracking, and loosely filled with fragments of broken porcelain to expose a large heated surface. This tube is gradually heated to redness in a charcoal furnace (fig. 158). One end of it receives the mixture of chlorine with steam, obtained by passing the

* *A portion of this* oxygen combines with chlorine, producing hypochlorous, and, *as recently stated,* perchloric acids.

ine evolved from hydrochloric acid and binoxide of manganese (p. 139), gh a flask (B) of boiling water. The other end of the tube is connected with tle (C) containing solution of potash to absorb any excess of chlorine and the chloric acid formed; from this bottle the oxygen is collected over the pneu- trough.

nce water is decomposed by chlorine, it is not surprising that most other ogen compounds are attacked by it. Ammonia (NH_3) is acted upon

Fig. 158.—Steam decomposed by chlorine.

th great violence. If a stream of ammonia gas issuing from a tube con- cted with a flask in which solution of ammonia is boiled (see fig. 111) passed into a bottle of chlorine, it takes fire immediately, burning th a peculiar flame, and yielding thick white clouds of hydrochlorate of monia; $4NH_3 + Cl_2 = 3(NH_3 . HCl) + N$. A piece of blotting- per dipped in strong ammonia, and immersed in a bottle of chlorine, ll exhibit the same effect. When the chlorine is allowed to act upon drochlorate of ammonia, its operation is less violent, and one of the st explosive substances is produced, which was formerly believed to be *hloride of nitrogen*, but is probably a compound formed by the removal part of the hydrogen from ammonia, and the substitution of chlorine ts stead.

Many of the compounds of hydrogen with carbon are also decomposed h violence by chlorine. When a piece of filter-paper is dipped oil of turpentine ($C_{20}H_{16}$), and afterwards into a bottle of chlorine, it sts into a red flame, liberating voluminous clouds of carbon and hydro- ric acid. Acetylene (C_4H_2) was found to explode spontaneously with rine when exposed to light (page 85). The striking decomposition of iant gas (C_4H_4) by chlorine on the approach of a flame has also n noticed (page 87). When a lighted taper is immersed in chlorine, es to burn, but with a small red flame, the hydrogen only of the ne combining with the chlorine, while the carbon separates in the chloric fume. When chlorine is [illegible] burning it renders the flame [illegible] ide of carbon (page 58). [illegible] the chlorine separates

When marsh-gas (C_2H_4) is diluted with an equal bulk of carbonic acid, to prevent violent action, and four volumes of chlorine added for each volume of marsh-gas, an oily liquid is gradually formed under the influence of daylight. This oily liquid is a mixture of chloroform and bichloride of carbon, the production of which is explained by the following equations:—

$$C_2H_4 + Cl_6 = 3HCl + \underset{\text{Chloroform.}}{C_2HCl_3}$$

$$C_2H_4 + Cl_8 = \underset{\text{Bichloride of carbon.}}{C_2Cl_4} + 4HCl.$$

It is evident from these equations that chlorine is capable, not only of removing hydrogen from a compound, but also of taking its place, equivalent for equivalent—a mode of action which gives rise to a very large number of chlorinated products from organic substances.

The attraction of chlorine for hydrogen enables the moist gas to act as an oxidising agent. Thus, if marsh-gas and chlorine be mixed in the presence of water, and exposed to daylight, the water is decomposed, its hydrogen combining with the chlorine, and its oxygen with the carbon of the marsh-gas; $C_2H_4 + 4HO + Cl_8 = 2CO_2 + 8HCl$.

103. The powerful bleaching effect of chlorine upon organic colouring matters is now easily understood. If a solution of chlorine in water be poured into solution of indigo (*sulphindigotic acid*) the blue colour of the indigo is discharged, and gives place to a comparatively light yellow colour. The presence of water is essential to the bleaching of indigo by chlorine, the dry gas not affecting the colour of dry indigo. The indigo is first oxidised at the expense of the water and converted into *isatine*, which is then acted upon by the chlorine and converted into *chlorisatine*, having a brownish yellow colour—

$$\underset{\text{Indigo.}}{C_{16}H_5NO_2} + 2HO + Cl_2 = \underset{\text{Isatine.}}{C_{16}H_5NO_4} + 2HCl.$$

$$\underset{\text{Isatine.}}{C_{16}H_5NO_4} + Cl_2 = \underset{\text{Chlorisatine.}}{C_{16}H_4ClNO_4} + HCl.$$

Nearly all vegetable and animal colouring matters contain carbon, hydrogen, nitrogen, and oxygen, and are converted by moist chlorine into products of oxidation or chlorination which happen to be colourless, or nearly so.

Fig. 159.

That dry chlorine will not bleach, may be shown by shaking some oil of vitriol in a bottle of the gas, and allowing it to stand for an hour or two, so that the acid may remove the whole of the moisture. If a piece of crimson paper be dried at a moderate heat and suspended in the bottle while warm, it will remain unbleached for hours, but a similar piece of paper suspended in a bottle of moist chlorine will be bleached almost immediately. If characters be written on crimson paper with a wet brush, and the paper placed in a jar beside a bottle of chlorine (fig. 159), it will be found, on removing the stopper, that white characters soon make their appearance on the red ground.

If a collection of coloured linen or cotton fabrics, or of artificial flowers, be exposed to the action of moist chlorine gas or of chlorine water, those which are dyed with organic colouring matters will be bleached at once, whilst the mineral colours will for the most part remain unaltered. Green leaves, immersed in chlorine, acquire a rich autumnal brown tint, and are eventually bleached. All flowers are very readily bleached by this gas.

Chlorine is very extensively employed for bleaching linen and cotton, the gas acting upon the colouring matter without affecting the fibre, but silk and wool present much less resistance to chemical action, and would be much injured by chlorine, so that they are always bleached by sulphurous acid.

Neither chlorine itself nor its solution in water can be very conveniently employed for bleaching on the large scale, on account of the irritating effect of the gas, so that it is usual to employ it in the form of *chloride of lime*, from which it can be easily liberated as it is wanted.

104. *Chloride of lime* or *bleaching powder* is prepared by passing chlorine gas into boxes of lead or stone in which a quantity of slaked lime is spread out upon shelves. The lime absorbs nearly half its weight of chlorine, and forms a white powder which has a very peculiar smell somewhat different from that of chlorine. The chloride of lime thus produced appears to consist of a mixture of *hypochlorite of lime* ($CaO.ClO$) with *oxychloride of calcium* ($CaCl.2CaO$), the action of chlorine upon hydrate of lime being represented by the following equation :—

$$\underset{\text{Hydrate of lime.}}{4\,(CaO.HO)} + Cl_2 = \underset{\text{Chloride of lime.}}{(CaO.ClO + CaCl.2CaO)} + 4HO\,.$$

When the chloride of lime is treated with water, the hypochlorite of lime ($CaO.ClO$) and chloride of calcium ($CaCl$) are dissolved, whilst hydrate of lime is left. If this solution be added to blue litmus, it will be found to exert little bleaching action, but on adding a little acid (sulphuric, for example), the blue colour will be discharged, the acid setting free the chlorine, which acts upon the colouring matter.

$$\underset{\text{Solution of Chloride of lime.}}{(CaO.ClO + CaCl)} + 2(HO.SO_3) = 2(CaO.SO_3) + 2HO + Cl_2\,.$$

Even carbonic acid will develope the bleaching property of chloride of lime, so that the above mixture may be decolorised by breathing into it through a glass tube.

When chloride of lime is used for bleaching on the large scale, the stuff to be bleached is first thoroughly cleansed from any grease or *weaver's dressing*, by boiling it in lime-water and in a weak solution of soda, and is then immersed in a weak solution of the chloride of lime. This by itself, however, exerts very little action upon the natural colouring matter of the fibre, and the stuff is therefore next immersed in very dilute sulphuric acid, when the colouring matter is so far altered as to become soluble in the alkaline solution in which it is next immersed, and a repetition of these processes, followed up by a thorough rinsing, generally perfects the bleaching.

The property possessed by acids of liberating chlorine from the chloride of lime is applied in calico-printing to the production of white patterns upon a red ground. The stuff having been dyed with Turkey red, the pattern is imprinted upon it with a *discharge* consisting of an acid (tartaric, phosphoric, or arsenic) thickened with gum. On passing the fabric through a bath of weak chloride of lime, the colour is discharged only at those parts to which the acid has been applied, and where, consequently, chlorine is liberated.

The explanation above given of the bleaching effect of chlorine may *probably be applied also to its so-called disinfecting* properties. The

atmosphere, in particular localities, is occasionally contaminated with poisonous substances, some of which are known only by their injurious effects upon the health, their quantity being so small that they do not appear in the results of the analysis of such air. Since, however, these substances appear to be acted upon by the same agents which are usually found to decompose organic compounds, they are commonly believed to be bodies of this class, and chlorine has been very commonly employed to combat these insidious enemies to health, since Guyton de Morveau, in the latter part of the last century, made use of it to destroy the odour arising from the bodies interred in the vaults beneath the cathedral of Dijon.

Among the offensive and unhealthy products of putrefaction of animal and vegetable matter, sulphuretted hydrogen, ammonia, and bodies similarly constituted, are found. That chlorine breaks up these hydrogen compounds is well known, and hence its great value for removing the unwholesome properties of the air in badly drained houses, &c.

Chloride of lime is one of the most convenient forms in which to apply chlorine for the purposes of fumigating and disinfecting. If a cloth saturated with the solution be suspended in the air, the carbonic acid causes a slow evolution of hypochlorous acid, which is even a more powerful disinfectant than chlorine itself. In extreme cases, where a rapid evolution of chlorine is required, the bleaching powder is placed in a plate, and diluted sulphuric acid is poured over it, or the powder may be mixed with half its weight of powdered alum in a plate, when a pretty rapid and regular escape of chlorine will ensue.

105. The discovery of chlorine and the discussions which ensued with respect to its real nature, contributed very largely to the advancement of chemical science. About the year 1770, the Swedish chemist Scheele (who afterwards discovered oxygen), first obtained chlorine by heating manganese ore with muriatic acid.

The construction which Scheele put upon the result of this experiment was one which was consistent with the chemistry of that date. He supposed the muriatic acid to have been deprived of *phlogiston*, and hence chlorine was termed by him *dephlogisticated muriatic acid*. This phlogiston had long been a subject of contention among philosophers, having been originally assumed to exist in combination with all combustible bodies, and to be separated from them during their combustion. Towards the decline of the phlogistic theory, attempts were made to prove the identity of this imaginary substance with hydrogen, which shows how very nearly Scheele's reasoning approached to the truth, even with the very imperfect light which he then possessed. Berthollet's movement was retrograde when, ten years afterwards, he styled chlorine *oxygenised muriatic* or *oxymuriatic acid*, but the experiments of Gay-Lussac and Thénard, and more particularly those of Davy in 1811, proved decisively that hydrochloric acid was composed of chlorine and hydrogen, and that the effect of the black oxide of manganese in Scheele's experiment was to remove the hydrogen in the form of water, thus setting the chlorine at liberty.

Hydrochloric Acid.

6. This acid is found in nature among the gases emanating from e volcanoes, and occasionally in the spring and river waters of vol- districts. For use it is always prepared artificially by the action lphuric acid upon common salt—

$$\underset{\text{Common salt.}}{NaCl} + HO.SO_3 = HCl + \underset{\text{Sulphate of soda.}}{NaO.SO_3}$$

odium of the common salt ging places with the hydro- f the sulphuric acid.

grains of common salt (pre- y dried in an oven) are intro- into a dry Florence flask (fig. to which has been fitted, by s of a perforated cork, a tube twice at right angles to allow as to be collected by downward cement. Six fluid drachms of sulphuric acid are poured the salt, and the cork having inserted, the flask is very heated in order to promote lisengagement of the hydro- ic acid gas, which is collected erfectly dry bottle, the mouth ich, when full, may be covered a glass plate smeared with a little grease. While being filled, the bottle may sed with a perforated card.

Fig. 160.—Preparation of hydrochloric acid gas.

mmon salt in powder sometimes froths to a very inconvenient extent with sul- c acid; it is therefore often preferable to employ fragments of fused salt, pre- by fusing the common salt in a clay crucible, and pouring on to a clean dry

more regular supply of hydrochloric acid gas is obtained from 1½ oz. of sal- oniac in lumps, and 1¼ oz. (measured) of sulphuric acid.

ıe bottle will be known to be filled with gas by the abundant escape he dense fumes which hydrochloric acid gas, itself transparent, pro- s by condensing the moisture of the air; for since the gas is much ier than air (sp. gr. 1·247), it will not escape in any quantity from ottle until the latter is full. The odour of the gas is very suffocat- but not nearly so irritating as that of chlorine.

ıe powerful attraction for water is one of most important properties of hydrochloric gas.

a jar of hydrochloric acid gas be closed with a plate and inverted under water, it will be found, moving the plate, that the gas is absorbed with rapidity, the water being forced up into the by the pressure of the external air in propor- ıs the gas is absorbed.

Florence flask is more convenient than a gas for this experiment. It must be perfectly dry, horoughly well filled with the gas, which may be ed to escape abundantly from the mouth. The delivering the hydrochloric acid gas must be y withdrawn, *so that the vacancy may be filled s and not by air. The flask is then closed* with the thumb, and opened under

Fig. 161.

water, which will enter it with great violence. The experiment may also be made as in the case of ammonia (fig. 161, see page 115).

The liquid hydrochloric, or *muriatic acid* of commerce, is a solution of the gas in water, and may be recognised by the grey fumes, with the peculiar odour of the acid, which it evolves when exposed to the air. One pint of water at a temperature of 40° F. is capable of absorbing 480 pints of hydrochloric acid gas, forming 1¼ pint of the solution, having the specific gravity 1·21. The strength of the acid purchased in commerce is usually inferred from the specific gravity, by reference to tables indicating the weight of hydrochloric acid contained in solutions of different specific gravities. The strongest hydrochloric acid (sp. gr. 1·21) contains 43 per cent. by weight of the gas. The common acid has usually a bright yellow colour, due to the accidental presence of a little perchloride of iron (Fe_2Cl_3), and not unfrequently smells of chlorine.

This acid is produced in enormous quantities in the alkali works, where common salt is decomposed by sulphuric acid in order to convert it into sulphate of soda, as a preliminary step to the production of carbonate of soda. The alkali manufacturer is compelled to condense the gas, for it is found to wither up the vegetation in the neighbourhood. For this purpose the hydrochloric acid gas is drawn up from the furnace through vertical cylinders filled with coke, over which streams of water are made to trickle. The water absorbs the acid, and is drawn off from below.

In preparing a pure solution of the acid for chemical use on a small scale, the gas prepared as above may be passed into a small bottle containing a very little water to wash the gas, or remove any sulphate of soda which may splash over, and then into a bottle about two-thirds filled with distilled water, the tube delivering the gas passing only about $\frac{1}{10}$ inch below the surface, so that the heavy solution of hydrochloric acid may fall to the bottom, and fresh water may be presented to the gas (fig. 162). For ordinary use, an acid of suitable strength is obtained by passing the gas from 6 ounces of common salt and 10 ounces of sulphuric acid into 7 (measured) ounces of water until its bulk has increased to 8 ounces. The bottle containing the water should be surrounded with cold water, since the absorption of hydrochloric acid by water is attended with evolution of heat.

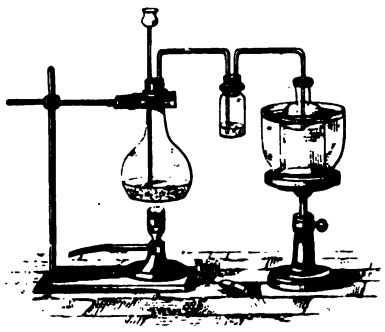


Fig. 162.—Preparation of solution of hydrochloric acid.

When the concentrated solution of hydrochloric acid is heated in a retort, it evolves abundance of hydrochloric acid gas, rendering it probable that it is not a true chemical compound of water with the acid. The evolution of gas ceases when the remaining liquid contains 20 per cent. of acid (and has a sp. gr. of 1·10). If a weaker acid than this be heated, it loses water until it has attained this strength, when it distils unchanged.*

The concentrated solution forms a very convenient source from which to procure the gas. It may be heated in a flask, and the gas dried by passing through a bottle filled with fragments of pumice-stone wetted with concentrated sulphuric acid, being collected over the mercurial trough (fig. 163).

* The proportion of acid thus retained by the water varies directly with the atmospheric pressure to which it is exposed during the distillation.

The avidity with which water absorbs hydrochloric acid is the more remarkable, because this gas can be liquefied only under a very high pressure, amounting at the ordinary temperature to about 40 atmospheres.

Fig. 163.

The liquefied hydrochloric acid has comparatively little action even upon those metals which decompose its aqueous solution with great violence; quick-lime is unaffected by it, and solid litmus dissolves in it with a faint purple colour, instead of the bright red imparted by the aqueous hydrochloric acid. (These facts answer the objection that anhydrous sulphuric acid (SO_3) cannot be considered an acid, because it has none of the powerful acid characters of oil of vitriol, since it cannot be doubted that hydrochloric acid is, in a chemical sense, an acid in its anhydrous state, though it manifests its acid properties only when water is present.)

The injurious action of hydrochloric acid gas upon growing plants is probably connected with its attraction for water. If a spray of fresh leaves is placed in a bottle of hydrochloric acid, it becomes at once brown and shrivelled.

107. *Action of hydrochloric acid upon metals.*—Those metals which have the strongest attraction for oxygen will also generally have the strongest attraction for chlorine, so that in respect to their capability of decomposing hydrochloric acid, they may be ranked in pretty nearly the same order as in their action upon water (p. 23). Since, however, the attraction of chlorine for the metals is generally superior to that of oxygen, the metals are more easily acted upon by hydrochloric acid than by water, the metal taking the place of the hydrogen, and a chloride of the metal being formed.

Even silver, which does not decompose water at any temperature, is dissolved, though very slowly, by boiling concentrated hydrochloric acid, the chloride of silver formed being soluble in the strong acid, though it may be precipitated by adding water.

Gold and platinum, however, are not attacked by hydrochloric acid, but if a little free chlorine be present, it converts them into chlorides.

Iron and zinc decompose the acid very rapidly in the cold, forming chlorides of iron and zinc, and liberating hydrogen: $Fe + HCl = FeCl + H$.

When potassium or sodium is exposed to hydrochloric acid gas, it immediately becomes coated with a white crust of chloride, which partly protects the metal from the action of the gas, but when these metals are heated to fusion in hydrochloric acid gas, they burn vividly—

$$Na + HCl = NaCl + H.$$

The composition of hydrochloric acid may be exhibited by confining a measured volume of the gas over mercury (see fig. 73, page 73), and passing up a freshly cut pellet of sodium. On gently agitating the tube, the gas diminishes in volume, and after a time will have contracted to one-half, and will be found to have all the properties of hydrogen. This result confirms that obtained by synthesis, as described above, that one volume of hydrochloric acid contains half a volume of hydrogen and half a volume of chlorine.

108. *Action of hydrochloric acid upon metallic oxides.*—As a general rule it may be stated, that when hydrochloric acid acts upon the oxide of a metal, the results are water and a chloride of the metal having a composition which corresponds to that of the oxide.

Thus, oxide of silver acted on by hydrochloric acid gives water and chloride of silver; $AgO + HCl = HO + AgCl$.

Suboxide of copper (cuprous oxide) yields water and subchloride of copper (cuprous chloride); $Cu_2O + HCl = HO + Cu_2Cl$.

Sesquioxide of iron gives water and sesquichloride of iron—

$$Fe_2O_3 + 3HCl = 3HO + Fe_2Cl_3 .$$

With binoxide of tin, water and bichloride of tin are obtained—

$$SnO_2 + 2HCl = 2HO + SnCl_2 .$$

Teroxide of antimony is converted into water and terchloride of antimony; $SbO_3 + 3HCl = 3HO + SbCl_3$.

In cases where the corresponding chloride does not exist, or is not stable under the conditions of the experiment, a chloride is formed containing less chlorine than is equivalent to the oxygen in the oxide, and the balance is evolved in the free state. Thus, when sesquioxide and binoxide of manganese are heated with hydrochloric acid—

$$\begin{aligned} Mn_2O_3 &+ 3HCl = 3HO + 2\,MnCl + Cl \\ MnO_2 &+ 2HCl = 2HO + MnCl + Cl \end{aligned}$$

since the sesquichloride and bichloride of manganese are decomposed by heat into the chloride (MnCl) and free chlorine.

Chromic acid, a chloride corresponding to which is not known to exist, when heated with hydrochloric acid, yields sesquichloride of chromium and chlorine—

$$2CrO_3 + 6HCl = 6HO + Cr_2Cl_3 + Cl_3 .$$

Every metallic protoxide (containing one equivalent of oxygen with one equivalent of a metal) has a corresponding chloride of a stable character, but the higher oxides less frequently form corresponding chlorides with any stability.

109. *Equivalent weights of hydrochloric acid and of chlorine.*—It is ascertained by experiment that 36·5 grains of hydrochloric acid are required to neutralise one equivalent (47 grains) of potash. The number 36·5, therefore, represents the equivalent weight of hydrochloric acid. When water is decomposed by chlorine (p. 142) 35·5 grains of chlorine are required to displace 8 grains (one equivalent) of oxygen, so that 35·5 is the equivalent weight of chlorine. By measuring 35·5 grains of chlorine, it found to occupy twice the volume of 8 grains of oxygen, so that if 1 valent of oxygen be represented to occupy one volume, 1 equivalent rine will occupy two volumes, like the equivalent of hydrogen.

It appears, then, that two volumes (one equivalent or 1 part by weight) of hydrogen combined with two volumes (one equivalent or 35·5 parts by weight) of chlorine, form four volumes (one equivalent or 36·5 parts by weight) of hydrochloric acid.

On the assumption that 1 part by weight of hydrogen represents 1 volume or 1 atom, 35·5 parts by weight of chlorine will also represent 1 volume or 1 atom, and these will unite to form 2 volumes or 1 molecule of hydrochloric acid. The molecular formula of hydrochloric acid is, therefore, identical with its equivalent formula, HCl.

110. *Types of atomic formulæ; atomicity.*—On examining the composition by volume of hydrochloric acid, water, ammonia, and marsh-gas, it is seen that equal volumes of these compounds, measured in the gaseous state at the same temperature and pressure, contain respectively, 1, 2, 3, and 4 volumes of hydrogen.

Thus 2 volumes of hydrochloric acid gas contain 1 volume of chlorine and 1 volume of hydrogen.
2 volumes of watery vapour contain 1 volume of oxygen and 2 volumes of hydrogen.
2 volumes of ammonia contain 1 volume of nitrogen and 3 volumes of hydrogen.
2 volumes of marsh-gas contain 1 volume (?) of imaginary carbon vapour and 4 volumes of hydrogen.

In the case of marsh-gas, it has been already explained that the volume occupied by a given weight of carbon vapour cannot be ascertained by experiment, but there are reasons to justify the assumption that 12 parts by weight of carbon vapour would occupy the same volume as 8 parts by weight of oxygen. In the other cases, the above statements exhibit the direct results of experiments previously described.

If it be allowed that one atom of each element occupies one volume, then hydrochloric acid, water, ammonia, and marsh-gas will contain, for one atom of chlorine, oxygen, nitrogen, and carbon, respectively, 1, 2, 3, and 4 atoms of hydrogen, or, taking the symbol for each element to represent one atom—

			Vols. H=1	Weights H=1
Hydrochloric acid	= ClH	= HCl	= 2	= 36·5
Water	= ΘHH	= $H_2Θ$	= 2	= 18
Ammonia	= NHHH	= H_3N	= 2	= 17
Marsh-gas	= CHHHH	= H_4C	= 2	= 16

Since, on the atomic theory, hydrogen is accepted as the unit of atomic weight and volume, it appears reasonable to fix upon it as representing the unit of combining power, and to classify the elements according to the tendency of their atoms to imitate the combining power of one or more atoms of hydrogen.

By the *atomicity* of an element, is meant the number expressing the hydrogen-atoms to which one atom (or volume) of that element is usually equivalent.

Thus, the atomicity of chlorine is = 1, for one volume (or atom) of this element not only combines with, and neutralises the properties of, one atom (or volume) of hydrogen, but is capable of representing, or occupying *the place of, one atom of hydrogen* in its compounds (see p. 144).

The atomicity of oxygen is = 2, since one volume (or atom) of oxygen combines with, and neutralises two atoms (or volumes) of hydrogen in water, and is generally capable of occupying the place of two atoms of hydrogen in the compounds of that element.

The atomicity of nitrogen is = 3, for one volume (or atom) of nitrogen neutralises the properties of three atoms (or volumes) of hydrogen in ammonia, and is often found to occupy the place of three atoms of hydrogen in its compounds.

The atomicity of carbon is = 4, for one volume (or atom) of *imaginary* carbon vapour is combined, in marsh-gas, with four atoms (or volumes) of hydrogen, and in its compounds with other elements, one atom of carbon is usually found representing four atoms of hydrogen.

Since hydrochloric acid, water, ammonia, and marsh-gas are the most conspicuous members of large classes of chemical compounds, they are often referred to as *types*, and the elements, chlorine, oxygen, nitrogen, and carbon, are taken as the representatives of the various classes into which the elements are divided according to their atomicities.

Chlorine is the type of one-atom elements (technically called *mon-atomic*, *uni-equivalent*, *monad* elements), the atomic weights of which are represented by the same numbers as their equivalent weights.

Oxygen is the type of two-atom elements (*di-atomic*, *bi-equivalent*, *dyad* elements), of which the number representing the equivalent weight is half of that which represents the atomic weight.

Equivalent of oxygen = O = 8.
Atom of oxygen = Θ = 16.

Nitrogen is the type of three-atom elements (*tri-atomic*, *ter-equivalent*, *triad* elements), of which the number representing the equivalent weight is commonly taken as identical with that which represents the atomic weight, though if the equivalentic system were rigorously carried out, the equivalent should be one-third of the atomic weight.

Carbon is the type of four-atom elements (*tetratomic*, *quadrequivalent*, *tetrad* elements), of which the number representing the equivalent weight ought to be one-fourth of that which expresses the atomic weight, whereas it is usually represented as half that number.

Equivalent of carbon = C = 6.
Atom of carbon = Θ = 12.

Such anomalies as these are unavoidable during the present transitional period through which chemistry appears to be passing towards the ultimate adoption of atomic (or molecular) formulæ in the place of equivalent formulæ, a change which offers dazzling prospects of advantage in speculative chemistry, but will probably be of less service in practice than the preservation of equivalent formulæ, so corrected as to remove the anomalies presented in some few cases.

The experience of the last few years seems to warrant the belief, that it will be long before experiment (the only possible final resort for the chemist) has so far removed the exceptions to the atomic formulæ which presented, in some cases, by the gaseous volumes and specific heats of ements, that these formulæ can be said to present us with so true of the actual results of experiment as to console us for the loss of simplicity and practical utility of the equivalent formulæ.

markable that the four elements, hydrogen, oxygen, nitrogen,

nd carbon, which compose the chief part of living matter, are respectively nonatomic, diatomic, triatomic, and tetratomic elements.

In speculations relating to the atomic structure of compounds, it is ow usual to represent graphically the atomicity of each element; thus a nonatomic element, like hydrogen, is represented as affording one point f attachment, which may be indicated by writing the symbol H—; a diatomic element, like oxygen, affords two points of attachment, as shown by writing its atomic symbol —O—; accordingly, to form water, the diatomic oxygen attaches to itself two atoms of hydrogen, as represented by the molecular formula H—O—H, whereas in the peroxide of hydrogen (H_2O_2) the second atom of oxygen is only held by one point of attachment, so that the graphic expression H—O—H—O— accounts at once for its tendency to decompose into water and free oxygen. A triatomic element, such as nitrogen, has three points of attachment $\rangle N—$, and thus in ammonia, attaches to itself three atoms of hydrogen $\begin{matrix} H \\ H \end{matrix}\rangle N—H$. The tetratomic element, carbon, affords four points of attachment $\rangle C\langle$ and thus marsh-gas (CH_4) is represented by $\begin{matrix} H \\ H \end{matrix}\rangle C\langle \begin{matrix} H \\ H \end{matrix}$, and carbonic acid ($CO_2$) by $O\langle\rangle C\langle\rangle O$.

Compounds of Chlorine with Oxygen.

111. It is worthy of notice that whilst chlorine and hydrogen so readily unite, there is no method by which chlorine can be made to combine in a direct manner with oxygen, all the compounds of these elements having been hitherto obtained only by indirect processes. An excellent illustration is thus afforded of the fact, that the more closely substances resemble each other in their chemical relations, the less will be their tendency to combine, for chlorine and oxygen are both highly electronegative bodies, and therefore, having both a powerful attraction for the electropositive hydrogen, their attraction for each other is of a very low order.

The following table exhibits the compounds formed by one equivalent of chlorine with different proportions of oxygen. Those distinguished by a note of interrogation have not been obtained in a separate state, though there is good reason for believing them to exist :—

Oxides of Chlorine.

Name.	Equivalent Formula.	By Weight.	
		Cl	O
Hypochlorous acid . .	ClO	35·5	8
Chlorous acid	ClO_3	35·5	24
Chloric peroxide . . .	ClO_4	35·5	32
Chloric acid ?	ClO_5	35·5	40
Perchloric acid ? . . .	ClO_7	35·5	56

112. *Hypochlorous acid* is of some practical interest as one of the constituents of *chloride of lime*, *chloride of soda*, and other bleaching compounds. It is prepared by passing dry chlorine gas over dry precipitated oxide of mercury, and condensing the product in a tube surrounded with a mixture of ice and salt—

$$\underset{\text{Oxide of mercury.}}{HgO} + Cl_2 = \underset{\text{Chloride of mercury.}}{HgCl} + ClO\,.$$

The hypochlorous acid is thus obtained as a deep red liquid, which boils at 19° F., evolving a yellow vapour thrice as heavy as air, and having a very powerful and peculiar odour. This vapour is remarkably explosive, the heat of the hand having been known to cause its separation into its constituents, when two volumes of the vapour yield two volumes of chlorine and one volume of oxygen. As might be expected, most substances which have any attraction for oxygen or chlorine will decompose the gas, sometimes with explosive violence. Even hydrochloric acid decomposes it; one volume of hypochlorous acid gas is entirely decomposed by two volumes of hydrochloric acid, yielding water and chlorine—

$$ClO + HCl = HO + Cl_2\,.$$

Hypochlorous acid is a powerful bleaching agent, both its chlorine and oxygen acting upon the colouring matter in the manner explained at page 144.

Hypochlorous acid is absorbed in large quantity by water. The solution may be very readily prepared by shaking the red oxide of mercury with water in a bottle of chlorine as long as the gas is absorbed. The greater part of the chloride of mercury which is produced, combines with the excess of oxide of mercury to form a brown insoluble oxychloride, whilst the hypochlorous acid and a little chloride of mercury remain in solution. This solution is a most powerful oxidising and bleaching agent; it erases writing ink immediately, and does not corrode the paper if it be carefully washed. Printing ink, which contains lamp-black and grease, is not bleached by hypochlorous acid, so that this solution is very useful for removing ink stains from books, engravings, &c.

The action of some metals and their oxides upon solution of hypochlorous acid is instructive. Iron seizes upon the oxygen, whilst the chlorine is liberated; copper takes both the oxygen and chlorine, whilst silver combines with the chlorine and liberates oxygen. Oxide of lead (PbO) removes the oxygen, becoming peroxide of lead (PbO_2), and liberating chlorine, but oxide of silver converts the chlorine into chloride of silver, and liberates the oxygen; $AgO + ClO = AgCl + O_2$.

The salts of hypochlorous acid, or *hypochlorites*, are not known in a pure state, but are obtained in solution by neutralising the solution of hypochlorous acid with bases. They are decomposed even by carbonic acid, with liberation of hypochlorous acid.

When the solution of a hypochlorite is boiled, it becomes converted into a mixture of chloride and chlorate; thus—

$$\underset{\text{Hypochlorite of potash.}}{3(KO\,.\,ClO)} = \underset{\text{Chlorate of potash.}}{KO\,.\,ClO_5} + \underset{\text{Chloride of potassium.}}{2KCl}\,.$$

change is turned to practical account in the manufacture of chlorate ash. It is much hindered by the presence of an excess of alkali.

The solution of hypochlorous acid itself, when exposed to light, is decomposed into chloric acid and free chlorine—

$$5\,ClO + HO = HO.ClO_5 + Cl_4$$

Chloride of lime (see p. 145) is the most important compound containing hypochlorous acid. Its formula has already been given as $CaO.ClO + CaCl.2CaO + 4Aq$, showing it to be a mixture of hypochlorite of lime with oxychloride of calcium. When this compound is distilled with a small quantity of diluted sulphuric acid, a solution of hypochlorous acid is obtained; but if an excess of acid be used, the chloride of calcium is decomposed, furnishing hydrochloric acid, which acts upon the hypochlorous acid, and free chlorine is the result. Alcohol, although capable of dissolving chloride of calcium, does not extract that salt from bleaching powder, because it is combined with lime; but an excess of water decomposes the compound of chloride of calcium with lime, and dissolves the former.

Bleaching powder is liable to decomposition when kept, its hypochlorite of lime evolving oxygen, and becoming converted into chloride of calcium, which attracts moisture greedily, and renders the bleaching powder deliquescent. It has been known to shatter the glass bottle in which it was preserved, in consequence of the accumulation of oxygen.

When a solution of a salt of manganese or cobalt is added to solution of chloride of lime, a black precipitate of binoxide of manganese or sesquioxide of cobalt is obtained, the oxide of manganese or of cobalt acquiring additional oxygen from the hypochlorite of lime, and forming an oxide which is indifferent, and does not remain in combination with the acid. If this precipitate be boiled with an excess of the solution of chloride of lime, it causes a rapid disengagement of oxygen in some manner that has not yet been clearly explained.

Large quantities of oxygen are easily obtained by adding a few drops of solution of nitrate of cobalt to solution of chloride of lime, and applying a gentle heat.

Hypochlorite of soda, which is very useful for removing ink, is prepared in solution by decomposing solution of chloride of lime with solution of carbonate of soda, and separating the carbonate of lime by filtration. The solution is generally called "chloride of soda."

113. *Chloric acid.*—This acid is appropriately studied here, since its compounds are usually obtained by the decomposition of the hypochlorites. The only compound of chloric acid which possesses any great practical importance is the chlorate of potash ($KO.ClO_5$), which is largely employed as a source of oxygen, as an ingredient of several explosive compositions, and in the manufacture of lucifer matches.

Chlorate of potash.—The simplest method of obtaining this salt consists in passing an excess of chlorine rapidly into a strong solution of hydrate of potash, when the liquid becomes hot enough to decompose the hypochlorite of potash first formed, into chloride of potassium, which remains in solution, and chlorate of potash, which is deposited in tabular crystals, the ultimate result being expressed by the equation—

$$6(KO.HO) + Cl_6 = KO.ClO_5 + 5KCl + 6HO.$$

If carbonate of potash or a weak solution of hydrate of potash be employed, the liquid will require boiling after saturation with chlorine, in order to *convert the hypochlorite into chlorate.*

The following proportions will be found convenient for the preparation of chlorate of potash on the small scale as a laboratory experiment. 800 grains of carbonate of potash are dissolved, in a beaker, with two measured ounces of water. 600 grains of common salt are mixed with 450 grains of binoxide of manganese, and very gently heated in a flask (fig. 164) with a mixture of 1½ ounce (measured) of strong sulphuric acid and 4 ounces (measured) of water, the evolved chlorine being passed through a rather wide bent tube into the solution of carbonate of potash.

Fig. 164.

At first no action will appear to take place, although the solution absorbs the chlorine; because the first portion of that gas converts the carbonate of potash into a mixture of hypochlorite of potash, chloride of potassium, and bicarbonate of potash, some crystals of which will probably be deposited—

$$4(KO.CO_2) + Cl_2 + 2HO = KCl + KO.ClO + 2(KO.HO.2CO_2).$$

On continuing to pass chlorine, these crystals will redissolve, and brisk effervescence will be caused by the expulsion of the carbonic acid from the bicarbonate of potash—

$$2(KO.HO.2CO_2) + Cl_2 = KCl + KO.ClO + 2HO + 4CO_2.$$

When this effervescence has ceased, and the chlorine is no longer absorbed by the liquid, the change is complete, the ultimate result being represented by the equation—

$$2(KO.CO_2) + Cl_2 = KCl + KO.ClO + 2CO_2.$$

The solution (which often has a pink colour, due to a little permanganate of potash) is now poured into a dish, boiled for two or three minutes, filtered, if necessary, from any impurities (silica, &c.,) derived from the carbonate of potash, and set aside to crystallise. The ebullition has converted the hypochlorite of potash into chlorate of potash and chloride of potassium—

$$3(KO.ClO) = KO.ClO_5 + 2KCl.$$

The latter being soluble in about three times its weight of cold water, is retained in the solution, whilst the chlorate of potash, which would require about sixteen times its weight of cold water to hold it dissolved, is deposited in brilliant rhomboidal tables. These crystals may be collected on a filter, and purified from the adhering solution of chloride of potassium by pressure between successive portions of filter-paper. If they be free from chloride of potassium, their solution in water will not be changed by nitrate of silver, which would yield a milky precipitate of chloride of silver if that impurity were present. Should this be the case, the crystals must be redissolved in a small quantity of boiling water and recrystallised.

The above processes for preparing the chlorate of potash are far from economical, since five-sixths of the potash are converted into chloride, being employed merely to furnish oxygen to convert the chlorine into chloric acid. In manufacturing chlorate of potash upon the large scale, a much cheaper material, lime, is used to furnish the oxygen, one equivalent of carbonate of potash being mixed with six equivalents of slaked lime, and the damp mixture saturated with chlorine. On treating the mass with boiling water, a solution is obtained which contains chlorate of potash and chloride of calcium, the latter, being very soluble, remains in the liquor from which the chlorate of potash crystallises on cooling. The ultimate result of the action of chlorine upon the mixture of carbonate of potash and lime is thus expressed—

$$KO.CO_2 + 6CaO + Cl_6 = KO.ClO_5 + 5CaCl + CaO.CO_2.$$

A still cheaper salt of potassium, the chloride, has recently been employed with great economy as a substitute for the carbonate of potash.

The solution of chloride of potassium is mixed with lime, and saturated with chlorine in close leaden tanks. The solution is filtered, evaporated nearly to dryness, and redissolved in hot water, when the chlorate of potash crystallises out on cooling. The chloride of calcium is precipitated by carbonate of soda to obtain *precipitated chalk*.

Anhydrous chloric acid (ClO_5) has never been obtained in the separate state; but its hydrate ($HO.ClO_5$) may be procured by decomposing a solution of chlorate of potash with hydrofluosilicic acid, when the potassium is deposited as an insoluble silico-fluoride, and hydrated chloric acid is found in the solution*—

$$KO.ClO_5 + \underset{\text{Hydrofluosilicic acid.}}{HF.SiF_2} = HO.ClO_5 + KF.SiF_2 .$$

On evaporating the solution at a temperature not exceeding 100° F., the hydrated chloric acid is obtained as a yellow liquid with a peculiar pungent smell.

In its chemical characters, hydrated chloric acid bears a very strong resemblance to hydrated nitric acid, but is far more easily decomposed. It cannot even be kept unchanged for any length of time, and at temperatures above 104° F. it is decomposed into perchloric acid, chlorine, and oxygen—

$$2(HO.ClO_5) = HO.ClO_7 + HO + Cl + O_3 .$$

Hydrated chloric acid is one of the most powerful oxidising agents. A drop of it will set fire to paper, and oxidises phosphorus (even the amorphous variety) with explosive violence.

Chlorates.—Chloric acid, like nitric, is monobasic, one equivalent (47 parts) of potash forming a neutral salt with 75·5 parts of imaginary anhydrous chloric acid (ClO_5). The chlorates resemble the nitrates in their oxidising power, but generally act at lower temperatures, in consequence of the greater facility with which the chlorates part with their oxygen.

A grain or two of chlorate of potash, rubbed in a mortar with a little sulphur, for example, detonates violently, evolving a powerful odour of chloride of sulphur. Chlorate of potash and sulphur were used in some of the first percussion caps, but being found to corrode the nipple of the gun, they gave place to the *anticorrosive caps* containing fulminate of mercury.

If a little powdered chlorate of potash be mixed, on a card, with some black sulphide of antimony, and wrapped up in paper, the mixture will detonate when struck with a hammer.

A mixture of this description is employed in the *friction tubes* used for firing cannon. These are small tubes (A, fig. 165) of sheet copper (for military) or of quill (for naval use), filled with gunpowder; in the upper part of the tube a small copper rasp (B) is tightly fixed across it, and on each side of the rasp a pellet is placed containing 12 parts of chlorate of potash, 12 of sulphide of antimony, and 1 of sulphur, these ingredients being worked up into a paste with a solution of an ounce of shellac in a pint of spirit of wine. The friction tube is fixed in the vent of the gun, and the copper rasp quickly withdrawn by a cord in the hands of the gunner, when the detonating pellets explode and fire the powder.

Fig. 165.

The earliest lucifer matches were tipped with a mixture of chlorate of potash, sulphide of antimony and starch, and were kindled by drawing them briskly through a doubled piece of sand-paper.

* 440 *grain measures of hydrofluosilicic acid* of sp. gr. 1078 will decompose 100 grains *of chlorate of potash.*

At high temperatures the chlorates act violently upon combustible bodies. A little chlorate of potash sprinkled upon red-hot coals causes a very violent deflagration. If a little chlorate of potash be melted in a deflagrating spoon, and plunged into a bottle or flask containing coal-gas (fig. 166), the salt burns with great brilliancy, its oxygen combining with the carbon and hydrogen in the gas, which becomes, in this case, the *supporter of combustion*. The flask may be conveniently filled with coal-gas by inverting it, and passing a flexible tube from the gas pipe up into it.

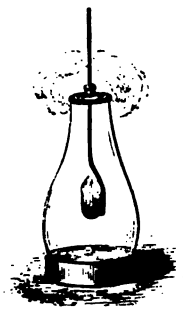


Fig. 166.

Chlorate of potash is much used in the manufacture of fireworks, especially as an ingredient of coloured fire compositions, which generally consist of chlorate of potash mixed with sulphur, and with some metallic compound to produce the desired colour in the flame. They are not generally made of the best quality on the small scale, from want of attention to the very finely powdered state of the ingredients, the absence of all moisture, and the most intimate mixture.

If these precautions be attended to, the following prescriptions will give very good coloured fires:—

Red fire.—40 grains of nitrate of strontia, thoroughly dried over a lamp, are mixed with 10 grains of chlorate of potash, and reduced to the finest possible powder. *In another mortar* 13 grains of sulphur are mixed with 4 grains of black sulphide of antimony (crude antimony). The two powders are then placed upon a sheet of paper, and very intimately mixed with a bone knife, avoiding any great pressure. A little heap of the mixture touched with a red-hot iron ought to burn with a uniform red flame, the colour being due to the strontium.

Blue fire.—15 grains of chlorate of potash are mixed with 10 grains of nitrate of potash and 30 grains of oxide of copper in a mortar. The finely-powdered mixture is transferred to a sheet of paper, and mixed, by a bone knife, with 15 grains of sulphur. The colour of the fire is given chiefly by the copper.

Green fire.—10 grains of chlorate of baryta are mixed with 10 grains of nitrate of baryta in a mortar, and afterwards, on paper, with 12 grains of sulphur. The barium is the cause of the bright green colour of the flame.

These compositions are rather dangerous to keep, since they are liable to spontaneous combustion.

White gunpowder is a mixture of two parts of chlorate of potash with one part of dried yellow prussiate of potash, and one part of sugar, which explodes very easily under friction or percussion.

The decomposition of chlorate of potash by heat into oxygen and chloride of potassium is attended with evolution of heat, unlike most cases of chemical decomposition, in which heat is generally absorbed. If chlorate of potash be heated to the point at which it begins to decompose, and a little peroxide of iron be thrown into it, enough heat will be evolved to bring the mass to a red heat, although the peroxide of iron is not oxidised. Experiment has shown that one part of chlorate of potash evolves, during decomposition, nearly 39 units of heat, or enough heat to raise 39 parts of water through 1° C. This anomalous evolution of heat must of course contribute to increase the energy of explosive mixtures containing the chlorate, and may be accounted for on the supposition, that the heat evolved by the combination of the potassium with the chlorine to form chloride of potassium exceeds that which is absorbed in effecting the chemical disintegration of the chlorate.

114. Anhydrous *perchloric acid* (ClO_7) is not known. The hydrated acid is obtained by evaporating down, at a boiling heat, the solution of chloric acid obtained by decomposing chlorate of potash with hydrofluosilicic acid (see p. 157), when the chloric acid is decomposed into perchloric acid, chlorine, and oxygen—

$$2(HO.ClO_5) = HO.ClO_7 + HO + Cl + O_3 .$$

When the greater part of the water has been boiled off, the liquid may be introduced into a retort and distilled. After the remainder of the water has passed over, it is followed by a heavy oily liquid which is $HO.ClO_7 + 4HO$. If this be mixed with four times its volume of strong sulphuric acid and again distilled, the pure hydrated perchloric acid ($HO.ClO_7$) first passes over as a yellow watery liquid. If the distillation be continued, the oily $HO.ClO_7 + 4HO$ distils over, and if this be mixed with the former and cooled, it yields silky crystals containing $HO.ClO_7 + 2HO$, which are decomposed at 230° F. into $HO.ClO_7$, which may be distilled off, and $HO.ClO_7 + 4HO$, which is left in the retort—

$$2(HO.ClO_7 + 2HO) = HO.ClO_7 + (HO.ClO_7 + 4HO) .$$

The pure hydrated perchloric acid is a colourless, very heavy liquid (sp. gr. 1·782), which soon becomes yellow from decomposition. It cannot be kept for any length of time. When heated it undergoes decomposition, often with explosion. In its oxidising properties it is more powerful than chloric acid. It burns the skin in a very serious manner, and sets fire to paper, charcoal, &c., with explosive violence. This want of stability, however, belongs only to the pure hydrate. If water be added to it heat is evolved, and a diluted acid of far greater permanence is obtained. Diluted perchloric acid does not even bleach, but reddens litmus in the ordinary way.

Perchloric acid is monobasic. The *perchlorates* are decomposed by heat, evolving oxygen, and leaving chlorides; thus—

$$\underset{\text{Perchlorate of potash.}}{KO.ClO_7} = KCl + O_8 .$$

The perchlorate of potash is always formed in the first stage of the decomposition of chlorate of potash by heat—

$$2(KO.ClO_5) = KO.ClO_7 + KCl + O_4 .$$

If a few crystals of chlorate of potash be heated in a test-tube, they first melt to a perfectly clear liquid, which soon evolves bubbles of oxygen. After a time the liquid becomes pasty, and if the contents of the tube, after cooling, be dissolved by boiling with water, the latter will deposit, as it cools, crystals of perchlorate of potash. These are readily distinguished from chlorate of potash by their not yielding a yellow gas (ClO_4) when treated with strong sulphuric acid. The perchlorate of potash is remarkable as one of the least soluble of the salts of potash, requiring 150 times its weight of cold water to dissolve it. Neither perchloric acid nor any of its salts is applied to any useful purpose.

115. *Chloric peroxide* or *peroxide of chlorine* is dangerous to prepare and examine on account of its great instability and violently explosive character. It is obtained by the action of strong sulphuric acid upon chlorate of potash—

$$\underset{\text{Chlorate of potash.}}{3(KO.ClO_5)} + \underset{\text{Sulphuric acid.}}{2(HO.SO_3)} = \underset{\text{Perchlorate of potash.}}{KO.ClO_7} + \underset{\text{Bisulphate of potash.}}{KO.SO_3, HO.SO_3} + \underset{\text{Chloric peroxide.}}{2ClO_4} + HO .$$

It is a bright yellow gas, with a chlorous and somewhat aromatic smell, and sp. gr. 2·32; condensible at −4° F. to a red, very explosive liquid. The gas is gradually decomposed into its elements by exposure to light, and a temperature of 140° F. causes it to decompose with violent explosion into a mixture of chlorine and oxygen, the volume of which is one-third greater than that of the compound.

On a small scale chloric peroxide may be prepared with safety by pouring a little

strong sulphuric acid upon one or two crystals of chlorate of potash in a test-tube supported in a holder. The crystals at once acquire a red colour, which gradually diffuses itself through the liquid, and the bright yellow gas collects in the tube. If heat be applied, the gas will explode, and the colour and odour of chloric peroxide will be exchanged for those of chlorine. If the chlorate of potash employed in this experiment contains chloride of potassium, explosion often takes place in the cold, since the hydrochloric acid evolved by the action of the acid upon that salt decomposes a part of the chloric peroxide, and thus provokes the decomposition of the remainder.

Fig. 167.

Chloric peroxide is easily absorbed by water, and the solution has powerful bleaching properties. Combustible bodies, such as sulphur and phosphorus, decompose the gas, as might be expected, with great violence. This powerful oxidising action of chloric peroxide upon combustible substances, appears to be the cause of the property possessed by mixtures of such substances with chlorate of potash to inflame when touched with strong sulphuric acid.

If a few crystals of chlorate of potash be thrown into a glass of water (fig. 167), one or two small fragments of phosphorus dropped upon them, and some strong sulphuric acid poured down a funnel tube to the bottom of the glass, the chloric peroxide will inflame the phosphorus with bright flashes of light and slight detonations.

Powdered sugar, mixed with chlorate of potash, on paper, will burn brilliantly when touched with a glass rod dipped in strong sulphuric acid. Matches may be prepared which inflame when moistened with sulphuric acid, by dipping the ends of splinters of wood in melted sulphur, and when cool, tipping them with a mixture of 5 grains of sugar and 15 grs. of chlorate of potash made into a paste with 4 drops of water. When dry they may be fired by dipping them into a bottle containing asbestos moistened with strong sulphuric acid. These matches, under the names of Eupyrion and Vesta matches, were used before the introduction of phosphorus into general use. The Promethean light was an ornamental scented paper spill, one end of which contained a small glass bulb of sulphuric acid surrounded with a mixture of chlorate of potash and sugar, which inflamed when the end of the spill was struck or squeezed, so as to break the bulb containing the sulphuric acid. The paper was waxed in order to make it inflame more easily. Percussion fuzes, &c., have been often constructed upon a similar principle.

Chloric peroxide used to be called hypochloric acid, but, like nitric peroxide, it appears to have no claim to be considered a true acid, since, in contact with the alkalies, it yields mixtures of chlorites and chlorates; thus—

$$2ClO_4 + 2KO = KO.ClO_3 + KO.ClO_5.$$

Euchlorine, the deep yellow, dangerously explosive gas evolved by the action of strong hydrochloric acid upon chlorate of potash, appears to be a compound of chloric and chlorous acids ($2ClO_5.ClO_3$) mixed with free chlorine.

116. *Chlorous acid* is another unstable and dangerously explosive gas, obtained by the action of a very gentle heat upon a mixture of three parts of arsenious acid, four of chlorate of potash, and sixteen of diluted nitric acid (sp. gr. 1·24)—

$$\underset{\text{Chlorate of potash.}}{KO.ClO_5} + \underset{\text{Nitric acid.}}{HO.NO_5} + \underset{\text{Arsenious acid.}}{AsO_3} + 2HO =$$

$$\underset{\text{Nitrate of potash.}}{KO.NO_5} + \underset{\text{Arsenic acid.}}{3HO.AsO_5} + \underset{\text{Chlorous acid.}}{ClO_3}$$

orous acid is a deep yellowish green heavy gas (sp. gr. 2·65) which

absorbed by water, and decomposed even more easily than the chloric oxide. It is a weak acid, its salts, the *chlorites*, being decomposed even by carbonic acid. A mixture of ice and salt does not liquefy chlorous acid, but an intense cold condenses it to a red liquid.

117. *General review of the oxides of chlorine.*—Several points of resemblance will have been noticed between the series of oxides of chlorine and those of nitrogen, but the former are much less stable than the latter. Chlorous acid (ClO_3), like nitrous acid (NO_3), is a weak acid; chloric peroxide (ClO_4) is easily resolved by bases into chlorous and chloric acids, just as nitric peroxide (NO_4) is resolved into nitrous and nitric acids. The hydrated chloric acid ($HO . ClO_5$) is a powerful oxidising agent like hydrated nitric acid ($HO . NO_5$), and the chlorates resemble the nitrates in their solubility in water and their oxidising power. The composition by volume of those oxides of chlorine which are known in the separate state, is exhibited in the following table:—

	Equivt. Formula.	Equivt. Weight.	Equivt. Volume.	By Volume.	
				Cl	O
Hypochlorous acid .	ClO	43·5	2	2	1
Chlorous acid . .	ClO_3	59·5	3	2	3
Chloric peroxide .	ClO_4	67·5	4	2	4

The relative volumes in which the chlorine and oxygen are united are the same, therefore, as in the corresponding oxides of nitrogen, but the equivalent volume of chlorous acid differs from that which is usually assumed for nitrous acid (see the table at p. 137).

On the hypothesis that each atom of an element occupies one volume, the molecular (atomic) formula of hypochlorous acid would be $Cl_2\Theta$, that of chlorous acid $Cl_2\Theta_3$, and that of chloric peroxide $Cl_2\Theta_4$, or, on the assumption that the compound molecule occupies only two volumes, $Cl\Theta_2$.

Some chemists refuse to regard the hypochlorites, chlorites, chlorates, and perchlorates as composed of basic oxides united with hypochlorous, chlorous, (*hypothetical*) chloric, and (*hypothetical*) perchloric acids respectively, but consider them as derived from (*hypothetical*) hydrated hypochlorous acid ($HO . ClO$ or $HClO_2$), (*hypothetical*) hydrated chlorous acid ($HO . ClO_3$ or $HClO_4$), hydrated chloric acid ($HO . ClO_5$ or $HClO_6$), and hydrated perchloric acid ($HO . ClO_7$ or $HClO_8$), by the substitution of metals for the hydrogen contained in those compounds. Thus hypochlorite of lime ($CaO . ClO$) would become $CaClO_2$, chlorate of potash ($KO . ClO_5$) would be $KClO_6$, &c.

Against the first view it may be plausibly advanced, that we are unacquainted with the compounds ClO_5 and ClO_7, and against the second, that $HClO_2$ and $HClO_4$ are at present unknown. Moreover, if these formulæ represented the true constitution of the acids, it would be expected that their solutions in water should tend to decompose into hydrochloric acid and free oxygen, which is not the case.

Chlorides of Carbon.

118. It has already been seen that chlorine has no direct attraction for carbon, the two elements not being known to enter into direct combination, but several chlorides of carbon may be obtained by the action of chlorine upon other compounds of carbon. Thus, if Dutch liquid ($C_2H_4Cl_2$), produced by the combination of olefiant gas with chlorine (p. 86), be acted upon with an excess of chlorine in sunlight, the whole of its hydrogen is removed in the form of hydrochloric acid, and an equivalent amount of chlorine is substituted for it, yielding the *sesquichloride of carbon* (C_4Cl_6)—

$$C_4H_4Cl_2 + Cl_8 = C_4Cl_6 + 4HCl .$$

Sesquichloride of carbon is a white crystalline solid, with an aromatic odour rather like that of camphor. It fuses at 320° F., and boils at 360°, subliming unchanged. It is not dissolved by water, but is soluble in alcohol and ether.

When the vapour of sesquichloride of carbon is passed through a tube containing fragments of glass heated to redness, it is decomposed into chlorine and a colourless liquid, which is the *protochloride of carbon* (C_4Cl_4). It has an aromatic odour, and boils at 248° F.; is heavier than water (sp. gr. 1·5), which does not dissolve it, and is soluble in alcohol and ether.

By passing the vapour of this protochloride of carbon through tubes heated to bright redness, it is decomposed into chlorine and *subchloride of carbon* (C_4Cl_2), which forms silky crystals almost free from odour, insoluble in water, but soluble in ether, and capable of being sublimed unchanged at a high temperature. It burns in air with a red smoky flame.

Bichloride of carbon (C_2Cl_4) has been mentioned (p. 144) as the

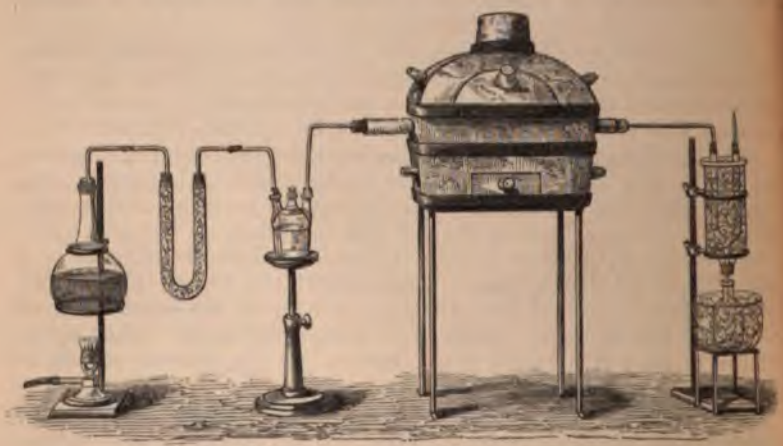


Fig. 168.—Preparation of bichloride of carbon.

final result of the action of chlorine upon marsh-gas (C_2H_4) and upon chloroform (C_2HCl_3). It is easily obtained in large quantity, by passing chlorine (dried by passing through a tube containing pumice wetted with strong sulphuric acid) (fig. 168) through a bottle containing bisulphide of carbon, and afterwards through a porcelain tube wrapped in sheet copper,

and filled with fragments of broken porcelain, maintained at a red heat by a charcoal or gas furnace, and condensing the products in a bottle surrounded by ice. A mixture of bichloride of carbon and subchloride of sulphur is thus obtained—

$$\underset{\text{Bisulphide of carbon.}}{2CS_2} + Cl_6 = \underset{\text{Bichloride of carbon.}}{C_2Cl_4} + \underset{\text{Subchloride of sulphur.}}{2S_2Cl}.$$

By shaking this mixture with solution of potash, the subchloride of sulphur is decomposed and dissolved, whilst the bichloride of carbon separates and falls to the bottom. The upper layer having been poured off, the bichloride may be purified by distillation.

Bichloride of carbon is a colourless liquid much heavier than water (sp. gr. 1·6), having a peculiar odour, and boiling at 172° F. It may be solidified at −9° F. The bichloride is insoluble in water, but dissolves in alcohol and ether.

By the action of chlorine on naphthaline ($C_{20}H_8$) Laurent obtained, as the ultimate result, a crystalline chloride of carbon containing $C_{20}Cl_8$, to which he gave the name *chlonaphthalise*.

It will be noticed that each of the compounds of chlorine with carbon, except the sesquichloride, has its parallel in the compounds of hydrogen with carbon;* thus—

Acetylene	C_4H_2	corresponds to	subchloride of carbon	C_4Cl_2
Olefiant gas	C_4H_4	,,	protochloride ,,	C_4Cl_4
Marsh-gas	C_2H_4	,,	bichloride ,,	C_2Cl_4

Indeed the principal reason for preferring these formulæ to the formulæ C_2Cl, CCl, and CCl_2, is that this correspondence may be exhibited, for since the chlorides of carbon are indifferent substances, it is not possible to obtain their equivalent weights by direct experiment, as in the case of bases or acids.

Composition by volume of the chlorides of carbon.—The composition of the chlorides of carbon, as determined by analysis, has been confirmed by the observation of their *vapour densities* (or specific gravities of their vapours), except in the case of the subchloride, of which the vapour density does not appear to have been correctly ascertained.

If it be assumed (see p. 81) that 6 parts by weight (1 eq.) of carbon, if converted into vapour, would occupy 2 vols. (O = 1 vol.), then the protochloride of carbon would contain 2 vols. of imaginary carbon vapour and 2 vols. of chlorine.

The specific gravity (or weight of 1 vol.) of imaginary carbon vapour being ·424, and that of chlorine 2·47—

2 vols. carbon vapour	would weigh	·848
2 vols. chlorine	,,	4·940
		5·788

The weight of 1 vol. (sp. gr.) of protochloride of carbon vapour has been found to be 5·82, which (allowing for experimental errors) is clearly the sum of these weights. Hence the weight of protochloride of carbon represented by the formula CCl occupies 1 vol., and contains 2 vols. of imaginary carbon vapour and 2 vols. of chlorine. But if the formula of olefiant gas be represented as C_4H_4 (28 parts by weight, occu-

* When vapour of protochloride of carbon is mixed with hydrogen, and passed through a red-hot tube, olefiant *gas and hydrochloric acid* are produced. The bichloride, under *similar circumstances, yields marsh-gas.*

pying 4 vols. ; O = 1 vol.), then the formula of protochloride of carbon must be C_4Cl_4 (166·0 parts by weight, occupying 4 vols. ; O = 1 vol.)

It has also been found that the weight of 1 volume (sp. gr.) of the vapour of sesquichloride of carbon is 8·157. But the sum of the weights of 4 vols. (2 eqs.) imaginary carbon vapour, and 6 vols. (3 eqs.) chlorine, would be 16·516, representing 2 vols. of C_2Cl_3. The formula C_4Cl_6, therefore, would represent 8 vols. of carbon vapour and 12 vols. of chlorine condensed into 4 vols. of sesquichloride of carbon.

The history of sesquichloride of carbon affords an instructive instance of the influence of the composition by volume of a compound upon its properties. By passing the vapour of bichloride of carbon through a tube heated to dull redness, a liquid is obtained which is found by analysis to contain precisely the same proportions of carbon and chlorine as the solid sesquichloride above described, but the specific gravity of its vapour is only 4·082, which is half that of the vapour of solid sesquichloride of carbon, showing that in the liquid compound the same proportions of carbon vapour and chlorine are condensed into a volume twice as large as in the solid sesquichloride, 4 vols. of the vapour of the liquid containing 4 vols. imaginary carbon vapour, and 6 vols. chlorine, and being represented by the formula C_2Cl_3.

The weight of 1 volume (sp. gr.) of vapour of bichloride of carbon is 5·3, which is the sum of 1 vol. imaginary carbon vapour and 2 vols. chlorine. The formula CCl_2, therefore, would represent (1 eq.) 2 vols. of carbon vapour and (2 eqs.) 4 vols. of chlorine condensed into 2 vols. of bichloride of carbon ; whilst C_2Cl_4 represents 4 vols. carbon and 8 vols. chlorine condensed into 4 vols. of bichloride of carbon.

Molecular formulæ of the chlorides of carbon.—If the atom of carbon (Ⓒ) be assumed to represent 12 parts by weight, and to occupy the same volume in the form of vapour as 1 part by weight of hydrogen (= 1 vol. or 1 atom), and 35·5 parts by weight of chlorine, which occupy the same volume as 1 part of hydrogen, be taken to represent one atom, the *molecular formulæ* of the chlorides of carbon would be—

Subchloride of carbon	$Ⓒ_2Cl_2$	corresponding to	$Ⓒ_2H_2$ acetylene.
Protochloride of carbon	$Ⓒ_2Cl_4$	,,	$Ⓒ_2H_4$ olefiant gas.
Sesquichloride of carbon (solid)	$Ⓒ_2Cl_6$		
,, ,, (liquid)	$ⒸCl_3$		
Bichloride of carbon	$ⒸCl_4$	,,	$ⒸH_4$ marsh-gas.

And each of these formulæ would represent twice the volume occupied by one atom of hydrogen, that is, would represent two volumes.

The following table exhibits the relations between the equivalent formulæ and the molecular formulæ of the chlorides of carbon :—

Chlorides of Carbon.

	Equivt. Formulæ.	Equivt. Volume.	Equivt. Weight.	Molecular Formulæ.	Molecular Volume.	Molecular Weight.
. . . . .	C_4Cl_2	4 ?	95·0	$Ⓒ_2Cl_2$	2 ?	95·0
. . . . .	C_4Cl_4	4	166·0	$Ⓒ_2Cl_4$	2	166·0
(solid), .	C_4Cl_6	4	237·0	$Ⓒ_2Cl_6$	2	237·0
liquid), .	C_2Cl_3	4	118·5	$Ⓒ_2Cl_3$	2	118·5
. . .		4	154·0	$Ⓒ_2Cl_4$	2	154·0

9. *Oxychloride of carbon, chlorocarbonic acid, or phosgene gas*, is pro-
d by the direct combination of equal volumes of carbonic oxide and
rine gases under the influence of sunlight (whence its last name),
n the mixture condenses to half its volume of a colourless gas, having
ry peculiar pungent smell, and fuming strongly when exposed to
t air, decomposing the moisture and producing hydrochloric acid;
Cl + HO = CO_2 + HCl. It is not a true acid, for it is de-
posed by bases, producing chlorides and carbonates. It is sometimes
d useful in chemical research for removing hydrogen from organic
pounds, and introducing carbonic oxide, or its elements, into its place.
ction on ammonia affords an example of this—

$$4(NH_3) + C_2O_2.Cl_2 = \underset{\text{Urea.}}{C_2O_2H_4N_2} + 2(\underset{\text{Hydrochlorate of ammonia.}}{NH_3.HCl})$$

hich two equivalents of NH_3 have been decomposed, two equivalents
he hydrogen having been removed in the form of hydrochloric acid,
replaced by two equivalents of carbonic oxide.
rom this and similar reactions, it is inferred that the true equivalent
ula of the oxychloride of carbon is $C_2O_2Cl_2$.

0. *Chloride of silicon*, unlike the chlorides of carbon, may be formed
he direct union of silicon with chlorine at a high temperature, but it
st prepared by passing dry chlorine over a mixture of artificial silica
charcoal, heated to redness in a porcelain tube connected with a
ver kept cool by a freezing-mixture. Neither carbon nor chlorine
rately will act upon the silica, but when they are employed to-
er, the carbon removes the oxygen and the chlorine combines with
ilicon—

$$SiO_2 + C_2 + Cl_2 = SiCl_2 + 2CO.$$

ie chloride of silicon is a colourless heavy liquid (sp. gr. 1·52) which
latile (boiling point, 138° F.), and fumes when exposed to air, the
ture of which decomposes it, yielding hydrochloric and silicic acids—

$$SiCl_2 + 2HO = SiO_2 + 2HCl.$$

hough it has received no practical application on a large scale, the
ide of silicon is valuable to the chemist as a convenient source of
ounds of silicon, which could not easily be procured from the very
angeable silicic acid.
e specific gravity (or weight of one volume) of vapour of chloride of
n is 5·87. Supposing it to be similarly constituted to the bichloride
rbon, this would contain 2 vols. of chlorine, and 1 vol. of imaginary
ur of silicon. Deducting the weight of 2 vols. chlorine (4·94) from
of 1 vol. of the chloride of silicon (5·87), there remains 0·93 for the
it of 1 vol. or sp. gr. of hypothetical vapour of silicon.
e formula $SiCl_2$ would represent 4 vols. of chlorine (2 eqs.) com-
with 2 vols. (1 eq.) of imaginary vapour of silicon, and condensed
space of two volumes.
ce $SiCl_2$ represents 14 parts by weight (1 eq.) of silicon combined
71 parts (2 eqs.) of chlorine, if the atom of silicon be assumed to
28 (see p. 109), it would be combined with 142 (4 atoms) of chlo-
and the atomic (molecular) formula of the chloride of silicon would
Cl_4 (Si = 28.) The silicon, here occupying the place of four atoms
drogen in hydrochloric acid, is often designated a *tetratomic* element

(see p. 151). Those chemists who regard silicic acid as SiO_3 of course represent the chloride of silicon as $SiCl_3$.

By passing hydrochloric acid over silicon heated to redness, a very remarkable liquid is obtained, which is much more volatile than the chloride of silicon (boiling point, 108° F.), and, unlike most chlorine compounds, is inflammable, burning with a greenish flame, and producing silica and hydrochloric acid. It fumes strongly in air, and is decomposed by water, yielding hydrochloric acid, and the substance termed leukone. The composition of this liquid appears to be $Si_3H_2Cl_5$, and its production would be represented by the equation $Si_3 + 5HCl = Si_3H_2Cl_5 + H_3$. Its decomposition by water would be explained by the equation—

$$Si_3H_2Cl_5 + 5HO = \underset{\text{Leukone.}}{Si_3H_2O_5} + 5HCl.$$

The *chloride of boron* (BCl_3) is similar in its general character to the chloride of silicon, and is prepared by a similar process, but it is a gas instead of a liquid at ordinary temperatures.

121. *Chloride of nitrogen* is the name usually given to the very explosive compound before referred to as being produced by the action of chlorine on sal-ammoniac. Its composition is somewhat uncertain; its explosive character rendering its exact analysis very difficult. Some chemists regard it as NCl_3, that is, ammonia in which all the hydrogen has been displaced by chlorine, whilst others believe it to contain hydrogen, regarding it as derived from two equivalents of ammonia ($NH_3 . NH_3$), by the substitution of five equivalents of chlorine for five of hydrogen ($NCl_3 . NHCl_2$).

It is a yellow, heavy, oily liquid (sp. gr. 1·65), which volatilises easily, yielding a vapour of very characteristic odour, which affects the eyes. When heated to about 200° F. it explodes with great violence, emitting a loud report and a flash of light. Its instability is, of course, attributable to the feeble attraction which holds its elements together; and the violence of the explosion, to the sudden expansion of a small volume of the liquid into a large volume of nitrogen, chlorine, and perhaps hydrochloric acid. As might be expected, its explosion is at once brought about by contact with substances which have an attraction for chlorine, such as phosphorus and arsenic; the oils and fats cause its explosion, probably by virtue of their hydrogen; oil of turpentine explodes it with greater certainty than the fixed oils. Alkalies also decompose it violently; whilst acids, having no action upon the chlorine, are not so liable to explode it. At 160° F. this substance has actually been distilled without explosion.

Although practically unimportant, the violent explosive properties of this substance render it so interesting that it may be well to give some directions for its safe preparation.

Preparation of chloride of nitrogen.—Dissolve 4 oz. of sal-ammoniac in 48 oz. (measured) of water, in a porcelain dish, at a gentle heat. Filter the solution, and pour it into a shallow *leaden* dish (A. fig. 169), previously cleaned from all grease by boiling a little solution of potash in it. Place in the solution a smaller leaden dish (B) (capacity, 1½ oz.), cleaned in the same way, and furnished with a copper wire handle.

Fig. 169.

Cut off the neck of a Florence flask (by scratching with a file, and leading the crack round with a red-hot iron), clean it by boiling a little potash in it, rinse it in water, and attach it to a string, so that it may be suspended, in an inverted position, upon a stand.

When the temperature of the solution of sal-ammoniac has fallen to nearly 90° F., fill the Florence flask with water in the pneumatic trough, and displace the water

by chlorine, passed up from a gas bottle free from grease. Close the flask with a watch-glass placed under the orifice, and suspend it by the string from a stand (fig. 170), so that its mouth may be about an inch below the surface of the solution of sal-ammoniac, and immediately over the centre of the small leaden dish. Remove the watch-glass, and let the whole arrangement be placed where the explosion can do no harm. The solution will soon begin to absorb the chlorine and to rise in the flask, whilst yellow oily globules form upon its surface, occasionally collecting into a larger one, which falls through the solution into the small leaden dish. When the flask is nearly filled with the solution, which will require about twenty minutes, gently raise the flask, from a distance, by hooking the string with a wire at the end of a long stick, and allow the solution to flow gently out of it into the leaden dish. Place the flask at a safe distance, lest there should be any chloride of nitrogen still clinging to it. Examine the leaden dishes to see where the oily globules have fallen, lifting out the smaller dish by hooking its wire handle with a long stick. Explode the globules from a safe distance with a stick dipped in turpentine. A good explosion will throw the solution up several feet, and will raise a large leaden dish several inches into the air, indenting it deeply at the seat of the explosion.

Fig. 170.

Another method of preparing the chloride, when it is not desired to examine it closely, but merely to witness the explosion, consists in acting upon sal-ammoniac with solution of hypochlorous acid; but as this does not succeed in a leaden vessel, and must be performed in glass or porcelain, the action should be conducted at a distance from the operator, lest he be wounded by the fragments of the vessel.

Fifty grains of red oxide of mercury are very finely powdered, and thrown into a pint bottle of chlorine together with ½ oz. (measured) of water. The stopper is replaced, and the bottle well shaken, loosening the stopper occasionally as long as the chlorine is absorbed. The solution of hypochlorous acid thus produced is filtered from the residual oxychloride of mercury, and poured into a clean *thumb-glass* (fig. 171). A lump of sal-ammoniac weighing 20 grains is then dropped into the solution, and the glass is placed in a safe situation where the explosion will do no harm. After the lapse of twenty minutes, the chloride of nitrogen may be exploded from a safe distance (9 feet) by touching it with a stick dipped in turpentine. The glass will be shattered into very small fragments, and the operator will be safer behind a screen, unless protected by a fencing-mask and leather gloves.

Fig. 171.

122. *Aqua regia.*—This name has been bestowed upon the mixture of (1 measure of) nitric, and (3 measures of) hydrochloric acid (*nitromuriatic acid*) which is employed for dissolving gold, platinum, and other metals which are not soluble in the separate acids. If a little gold leaf be placed in hydrochloric and nitric acids contained in separate glasses, the metal will remain unaffected even on warming the acids, but if the contents of the glasses be mixed, the gold will be immediately dissolved by the chlorine which is liberated in the action of the acids upon each other—

$$HO.NO_3 + 3HCl = 4HO + \underset{\text{Chloronitric gas.}}{NO_2Cl_2} + Cl .$$

The *chloronitric gas* which is formed does not act upon the gold, but is evolved as a red gas, condensable in a freezing mixture to a dark red liquid. It has a very peculiar odour, and is decomposed by contact with water into hydrochloric acid and nitric peroxide—

$$NO_2Cl_2 + 2HO = 2HCl + NO_4 .$$

A similar, though somewhat less volatile substance, called *chloronitrous gas, and having the formula NO_2Cl, is produced* by mixing 2 volumes of nitric

oxide with 1 volume of chlorine; it condenses to a red liquid at 0° F.; it is also produced in small quantity by the action of hydrochloric acid on nitric acid; $HO.NO_5 + 3HCl = 4HO + NO_2Cl + Cl_2$.

BROMINE.

123. It generally happens that elements between which any strong family likeness exists are found associated in nature. This remark particularly applies to the three elements—chlorine, bromine, and iodine, all of which are found in sea water, though the first predominates to such an extent that the others for a long time escaped notice. Bromine was brought to light in the year 1826 by Balard in the examination of *bittern*, which is the liquid remaining after the chloride of sodium and some other salts have been made to crystallise by evaporating sea water, which contains only about one grain of bromine per gallon, in the forms of bromide of magnesium and bromide of sodium. It is also extracted from the waters of certain mineral springs, as those of Kreuznach and Kissingen, which contain much larger quantities of bromine, either as bromide of potassium or of sodium or magnesium.

In extracting the bromine from these waters, advantage is taken of the circumstance that chlorine is capable of displacing bromine from its combinations with the metals. After most of the other salts, such as chloride of sodium, sulphate of soda, and sulphate of magnesia, which are less soluble than the bromides, have been separated from the water by evaporation and crystallisation, the remaining liquid is subjected to the action of chlorine gas, when it acquires an orange colour, due to the liberation of the bromine; $KBr + Cl = KCl + Br$. The bromine thus set free exists now diffused through a large volume of water, which cannot be separated from it in the usual way by evaporation, because bromine is itself very volatile. An ingenious expedient is therefore resorted to of shaking the orange liquid briskly with ether, which has a greater solvent power for bromine than is possessed by water, and therefore abstracts it from the aqueous solution; since ether does not mix to any great extent with water, it now rises to the surface of the liquid, forming a layer of a beautiful orange colour, due to the bromine which it holds in solution. This orange layer is carefully separated, and shaken with solution of potash, which immediately destroys the colour by removing the bromine, leaving the ether to rise to the surface in a pure state, and fit to be employed for abstracting the bromine from a fresh portion of the water. The action of the bromine upon potash is precisely similar to that of chlorine—

$$6KO + Br_6 = \underset{\text{Bromide of potassium.}}{5KBr} + \underset{\text{Bromate of potash.}}{KO.BrO_5}.$$

After the solution of potash has been several times shaken with the ethereal solution of bromine, and has become highly charged with this element, it is evaporated so as to expel the water, leaving a solid residue containing the bromide of potassium and bromate of potash. This saline mass is strongly heated to decompose the bromate of potash, and convert it into bromide of potassium—

$$KO.BrO_5 = KBr + O_6.$$

From this salt the bromine is extracted by distilling it with binoxide of

manganese and sulphuric acid, when the potassium is oxidised at the expense of the binoxide of manganese, and the bromine is liberated and condensed in a receiver kept cool by iced water—

$$KBr + MnO_2 + 2(HO.SO_3) = KO.SO_3 + MnO.SO_3 + 2HO + Br.$$

The aspect of the bromine so produced is totally different from that of any other element, for it distils over in the liquid condition, and preserves that form at ordinary temperatures, being the only liquid non-metallic element. Its dark red-brown colour, and the peculiar orange colour of the vapour which it exhales continually, are also characteristic; but, above all, its extraordinary and disagreeable odour, from which it derives its name (*βρῶμος, a stench*), leaves no doubt of its identity. The odour has some slight resemblance to that of chlorine, but is far more intolerable, often giving rise to great pain, and sometimes even to bleeding at the nose.

Liquid bromine is thrice as heavy as water (sp. gr. 2·96), and boils at 145° F., yielding a vapour 5½ times as heavy as air (sp. gr. 5·54). It may be frozen at 9°·5 F. to a brown crystalline solid. It requires 33 times its weight of cold water to dissolve it, and is capable of forming a crystalline hydrate (Br + 10HO) corresponding to hydrate of chlorine.

In its bleaching power, its aptitude for direct combination, and its other chemical characters, it very closely resembles chlorine—so closely, indeed, that it is difficult to distinguish, in many cases, between the compounds of chlorine and bromine with other substances, unless the elements themselves be isolated. A necessary consequence of so great a similarity is, that very little use has been made of bromine, since the far more abundant chlorine fulfils nearly all the purposes to which bromine might otherwise be applied. In the daguerreotype and photographic arts, however, some special applications of bromine have been discovered, and for some chemical operations, such as the determination of the illuminating hydrocarbons in coal-gas, bromine is sometimes preferred to chlorine. In the composition of their compounds, chlorine and bromine also exhibit great analogy.

Hypobromous acid (BrO) has not been obtained in the anhydrous state, but its solution in water may be obtained by shaking oxide of mercury with water and bromine. The solution is very unstable, decomposing, especially when heated, with liberation of bromine and formation of bromic acid. The action of bromine upon diluted solutions of the alkalies, and upon the alkaline earths, produces bleaching liquids similar to those formed by chlorine.

Anhydrous bromic acid (BrO_5) has never been obtained, but *hydrated bromic acid* ($HO.BrO_5$) can be prepared in a similar manner to hydrated chloric acid, to which it has a great general resemblance, the bromates being also similar to the chlorates.

124. *Hydrobromic acid.*—The inferiority of bromine to chlorine in chemical energy is well exemplified in its relations to hydrogen, for the vapour of bromine mixed with hydrogen will not explode under the action of flame or of the electric spark, like the mixture of chlorine and hydrogen. Direct combination may, however, be slowly induced by contact with heated platinum.

When it is attempted to prepare this acid by distilling bromide of sodium or potassium with sulphuric acid (as in the preparation of hydrochloric acid), *the inferior stability of* hydrobromic acid is shown by the

decomposition of a part of it, the hydrogen being oxidised by the sulphuric acid, and the bromine set free; $HBr + HO.SO_3 = 2HO + SO_2 + Br$.

If a strong solution of phosphoric acid be employed instead of the sulphuric, pure hydrobromic acid may be obtained.

But the most instructive method of obtaining hydrobromic acid consists in attacking water with bromine and phosphorus simultaneously, when the phosphorus takes the oxygen of the water, forming phosphorous acid, and the bromine combines with the hydrogen to form hydrobromic acid—

$$6HO + Br_3 + P = 3HO.PO_3 + 3HBr .$$

Hydrated phosphorous acid.

Probably bromide of phosphorus (PBr_3) is formed as an intermediate stage.

The experiment may be made in a W-formed tube (fig. 172), one bend of which contains 40 grains of phosphorus in fragments intermingled with glass moistened with water, whilst the other bend contains 240 grains of bromine (about one drachm). This limb of the tube is corked, and the other furnished with a delivery tube, so that the gas may be collected either by downward displacement or over mercury. The bromine is slightly heated, when it distils over to the moist phosphorus, and hydrobromic acid is evolved. A moderate heat should afterwards be applied to the moist glass, to expel part of the hydrobromic acid from the water.

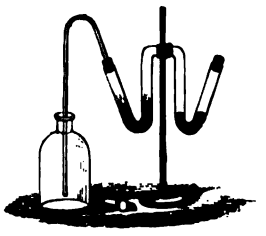


Fig. 172.—Preparation of hydrobromic acid.

Hydrobromic acid is very similar to hydrochloric acid; it liquefies at − 92° F., and has been solidified by a still lower temperature, which is not the case with hydrochloric acid. Like that gas it is very soluble in water, and the solution acts upon metals and their oxides in the same manner as hydrochloric acid. Chlorine removes the hydrogen from hydrobromic acid, liberating bromine, which it converts into *chloride of bromine* if employed in excess.

The composition of hydrobromic acid corresponds to that of hydrochloric. It contains 80 parts by weight (1 eq.) of bromine, combined with 1 part (1 eq.) of hydrogen, or 2 vols. of bromine vapour, combined with 2 vols. of hydrogen to form 4 vols. of hydrobromic acid.

Bromide of nitrogen has been obtained by the action of bromide of potassium upon chloride of nitrogen, which it resembles in general character and explosive properties.

Chloride of bromine is a very volatile yellow liquid of pungent odour. Its composition is not certainly known. That chlorine should unite directly with bromine, which it so much resembles in chemical character, illustrates its great tendency to direct chemical combination.

IODINE.

125. Iodine is contained in sea water in even smaller quantity than bromine, but the iodide of sodium appears to constitute a portion of the necessary food of certain varieties of sea-weed, which extract it from the sea water, and concentrate it in their tissues. The ash remaining after sea-weed has been burnt was long used, under the name of *kelp*, in soap-making, because it contains a considerable quantity of carbonate of soda; and in the year 1811, Courtois, a soap-boiler of Paris, being engaged in the manufacture of soda from kelp, obtained from the waste liquors a

substance which possessed properties different from those of any form of matter with which he was acquainted. He transferred it to a French chemist, Clement, who satisfied himself that it was really a new substance, and Gay-Lussac and Davy having examined it still more closely, it took its rank among the non-metallic elementary substances, under the name of iodine (*ἰώδης, violet coloured*), conferred upon it in allusion to the magnificent violet colour of its vapour.

This history of the discovery of iodine affords a very instructive example of the advantage of training persons engaged in manufactures to habits of accurate observation, and, if possible, of accurate chemical observation; for had Courtois passed over this new substance as accidental, or of no consequence, the community would have lost, at least for some time, the benefits derived from the discovery of iodine.

For some years the new element was only known as a chemical curiosity, but an unexpected demand for it at length arose on the part of the physician, for it had been found that the efficacy of the ashes of sponge, which had long been used in some particular maladies, was due to the small quantity of iodine which they contained, and it was, of course, thought desirable to place this remedy in the hands of the medical profession in a purer form than the ash of sponge, where it is associated with very large quantities of various saline substances. Much more recently the demand for this element has greatly increased, on account of its employment in photography, and large quantities of it are annually produced from kelp, the collection and burning of which affords occupation to the very poor inhabitants of some parts of the coasts of Ireland and Scotland, who would otherwise have been thrown out of work when soda began to be manufactured from common salt, and the demand for kelp as the source of that alkali had ceased. The sea-weed is spread out to dry, and burnt in shallow pits at as low a temperature as possible, for the iodide of sodium is converted into vapour and lost if the temperature be very high.* The ash, which is left in a half-fused state, is broken into fragments and treated with hot water, which dissolves about half of it, leaving a residue, consisting of carbonate and sulphate of lime, sand, &c. The whole of the iodide of sodium is contained in the portion dissolved by the water, but is mixed with much larger quantities of sulphate of soda, carbonate of soda, chloride of potassium, hyposulphite of soda, and sulphide of sodium. A portion of the water is expelled by evaporation, when the sulphate of soda, carbonate of soda, and chloride of potassium, being far less soluble than the iodide of sodium, crystallise out. In order to decompose the hyposulphite of soda and the sulphide of sodium, the liquid is mixed with an eighth of its bulk of oil of vitriol, which decomposes these salts, evolving sulphurous and hydrosulphuric acid, with deposition of sulphur, and forming sulphate of soda, which is deposited in crystals. The liquor thus prepared is next mixed with binoxide of manganese, and heated in a leaden retort (fig. 173), placed in a sand-bath, when the iodine is evolved as a magnificent purple vapour, which condenses in the globular glass receivers in the form of dark grey scales with metallic lustre, and having considerable resemblance to black lead. The liberation of the iodine is explained by the following equation—

$$NaI + MnO_2 + 2(HO.SO_3) = NaO.SO_3 + MnO.SO_3 + 2HO + I.$$

* *The sea-weed is often only charred and not incinerated, so as to avoid loss of iodine.*

The distillation is conducted at a temperature below 212°, to avoid the liberation of chlorine from the chloride of sodium, and the consequent formation of chloride of iodine.

Several processes have been devised to render the extraction of the iodine from the concentrated solution of kelp easier and more economical. The most promising is very similar to that employed for separating bromine (p. 168). The iodine is liberated by chlorine, and extracted from the liquid by shaking it with benzole; by treating the benzole with solution of potash, the iodine is converted into a mixture of iodide of potassium and iodate of potash, from which the iodine may be precipitated by acidifying with hydrochloric acid.

$$6KO + I_6 = 5KI + KO.IO_5$$
$$5KI + KO.IO_5 + 6HCl = 6KCl + 6HO + I_6.$$

The features of this element are extremely well marked; its metallic lustre and peculiar odour sufficiently distinguish it from all others, and the effect of heat upon it is very striking, in first easily fusing it (at 225° F.), and afterwards converting it (boiling point, 347° F.) into the most exquisitely purple vapour, which is nearly nine times as heavy as air (sp. gr. 8·72), and condenses upon a cool surface in shining scales. It stains the skin intensely brown if handled. The specific gravity of solid iodine is 4·95.

Fig. 173.—Extraction of iodine.

When iodine is shaken with cold water a very small quantity is dissolved, forming a light brown solution. Hot water dissolves a larger quantity, but alcohol is one of the best solvents for iodine, producing a dark red-brown solution (*tincture of iodine*) from which part of the iodine may be precipitated by adding water. A solution of iodide of potassium also dissolves iodine freely. Benzole and bisulphide of carbon dissolve it abundantly, producing fine violet-red solutions, which deposit the iodine, if allowed to evaporate spontaneously, in minute rhombic octahedral crystals aggregated into very beautiful fern-like forms. If an extremely weak aqueous solution of iodine be shaken with a little bisulphide of carbon, the latter will remove the iodine from the solution, and on standing, will fall to the bottom of the liquid, having a beautiful violet colour. By dissolving a large quantity of iodine in bisulphide of carbon, a solution is obtained which is perfectly opaque to rays of light, though it allows heat-rays to pass freely, and is, therefore, of great value in physical experiments. A solution of iodine in bichloride of carbon is also used for the same purpose.

Existing, as iodine does, in very minute quantity in the water from various natural sources, it would often be overlooked if the chemical analyst did not happen to possess a test of the most delicate description for it.

Iodine, in the uncombined state, dyes starch of a beautiful blue colour,

s may be proved by heating a grain or two of the element with water, nd adding to the solution a little thin starch (see p. 15), or by placing a inute fragment of iodine in a stoppered bottle, and suspending in it a iece of paper dipped in thin starch. This test, however, though sensi- ive to the smallest quantity of free iodine, gives no indication whatever ith iodine in combination, as it always exists in nature; in order, there- ore, to test for iodine, a little starch-paste is added to the suspected iquid, and then a drop of a weak solution of chlorine, which will set free he iodine, and cause the production of the blue colour. Characters ritten on paper with a brush dipped in a mixture of iodide of potassium nd starch, are brought out in blue by pouring a little chlorine-gas upon hem. It is necessary, however, carefully to avoid adding too much chlo- ine, since it would immediately destroy the colour of the iodised starch. Alkalies also bleach it, and the colour of a mixture of the iodised starch ith water is removed by heating, but returns in great measure when the olution cools.

Though very closely connected with chlorine and bromine in its gene- al chemical relations, there are several points in the history of iodine which ause it to stand out in marked contrast by the side of these elements. The ttraction which binds it to hydrogen and the metals is certainly weaker han that exerted by chlorine and bromine, so that either of these is cap- ble of displacing it from its compounds, and its bleaching properties are ery feeble. On the other hand, it exhibits a more powerful tendency to mite with oxygen, for boiling nitric acid converts it into iodic acid (IO_5), hough this oxidising agent would not affect chlorine or bromine.

Some of the compounds of iodine with the metals are remarkable for their beauti- ful colours. The *iodide of mercury*, produced by mixing solutions of iodide of potas- sium and chloride of mercury, forms a fine scarlet precipitate, which dissolves in an xcess of iodide of potassium to a *colourless* solution.

If this iodide of mercury be collected on a filter, washed and dried, it will be found, on heating a portion of it in a test-tube, that it acquires a fine yellow colour and sublimes in golden yellow crystals, which resume the original red colour when rubbed with a glass rod. If it be spread upon paper and gently heated, the scarlet iodide becomes yellow, but the red colour returns on rubbing it with the thumb- nail. These changes of colour are attended by an alteration in crystalline form, but not in the chemical composition of the iodide of mercury.

Iodide of lead has a bright yellow colour, as may be seen by precipitating iodide of potassium with a solution of acetate of lead. The precipitate is dissolved by boiling with water (especially on adding a little hydrochloric acid), forming a colour- less solution, from which the iodide of lead crystallises in very brilliant golden scales n cooling. *Iodide of silver* is produced as a yellow precipitate when nitrate of silver s added to iodide of potassium. The bromide and chloride of silver would form hite precipitates.

126. *Oxides of iodine.*—Although the compound IO, corresponding to ypochlorous acid, is believed to exist, it has never yet been obtained in a parate state, the only known oxides of iodine being iodic acid (IO_5) and riodic acid (IO_7?) which has only been obtained in the hydrated state.

Iodic acid, like the corresponding chloric and bromic acids, is formed hen iodine is dissolved in solution of potash or soda—

$$6KO + I_6 = KO.IO_5 + 5KI.$$

is most easily prepared by boiling iodine with the strongest nitric acid a long-necked flask, when it is dissolved in the form of iodic acid which left on evaporating the nitric acid, as a white mass. This may be puri- d *by dissolving in water and crystallising*, when the iodic acid forms

white hexagonal tables, which have the composition $HO.IO_5 + 2Aq$. Heated to 266° F., they become $HO.IO_5$, and at 360° F. the whole of the water is expelled, leaving anhydrous iodic acid, which is decomposed at about 700° F. into iodine and oxygen. The anhydrous iodic acid oxidises combustible bodies, but not with any great violence. The hydrate is far more stable than the hydrated chloric and bromic acids. Its solution first reddens litmus paper, and afterwards bleaches it by oxidation. Its salts, the *iodates*, are less easily soluble in water than the chlorates and bromates, which they resemble in their oxidising action upon combustible bodies. They are all decomposed by heat, evolving oxygen, and sometimes even iodine, showing how much inferior this element is to chlorine and bromine in its attraction for metals.

It is a remarkable feature of the iodates, that some of them contain two or even three equivalents of iodic acid to one of base. Thus there are three iodates of potash, $KO.IO_5$, $KO.2IO_5$, and $KO.3IO_5$. No such compounds are known in the cases of chloric and bromic acids.

Periodic acid has not been satisfactorily obtained in the anhydrous state. The hydrated periodic acid is obtained from the basic periodate of soda formed by passing chlorine through a mixture of iodate of soda and free soda, when the latter is decomposed, its sodium being abstracted by the chlorine, whilst its oxygen converts the iodic acid into periodic acid—

$$NaO.IO_5 + 3NaO + Cl_2 = \underset{\text{Basic periodate of soda.}}{2NaO.IO_7} + 2NaCl.$$

This periodate of soda is deposited, being sparingly soluble in water, a most unusual circumstance with salts of soda. By dissolving it in nitric acid, and adding nitrate of silver, a basic periodate of silver is obtained, which is yellow when precipitated from cold, and red from hot solutions—

$$2NaO.IO_7 + 2(AgO.NO_5) = \underset{\text{Basic periodate of silver.}}{2AgO.IO_7} + \underset{\text{Nitrate of soda.}}{2(NaO.NO_5)}.$$

When the silver salt is dissolved in nitric acid, it is decomposed into nitrate of silver, which remains in solution, and neutral periodate of silver, which is deposited in crystals—

$$2AgO.IO_7 + HO.NO_5 = AgO.IO_7 + AgO.NO_5 + HO.$$

When neutral periodate of silver is boiled with water, it again yields the insoluble basic periodate of silver, and hydrated periodic acid is found in the solution—

$$2(AgO.IO_7) + HO = 2AgO.IO_7 + HO.IO_7.$$

On evaporating the solution, the hydrated periodic acid is deposited in prismatic crystals having the composition $HO.IO_7 + 4Aq$, which lose their water at about 320° F., and are decomposed into iodic acid and oxygen at 400° F. The solution of periodic acid, of course, exhibits oxidising properties.

The *periodates* are remarkable for their sparing solubility in water; they are easily decomposed by heat, like the iodates. It will have been remarked, in the above account of the preparation of periodic acid, that his acid exhibits a great tendency to the formation of basic salts, whilst lic acid is remarkable for its acid salts.

27. *Hydriodic acid.*—Iodine vapour combines with hydrogen, under

the influence of heated platinum, to form hydriodic acid gas. The gas is best prepared by decomposing water with iodine in the presence of phosphorus, so as to produce hydriodic acid and phosphoric acid, which is allowed to act upon iodide of potassium in order to produce more hydriodic acid—

$$8HO + I_2 + P = 5HI + 3HO.PO_5 \text{ and}$$
$$2KI + 3HO.PO_5 = 2HI + 2KO.HO.PO_5 .$$
Phosphate of potash.

100 grains of iodide of potassium are dissolved in 50 grains of water in a retort (fig. 174), and 200 grains of iodine are added; when this has dissolved, 10 grains of phosphorus are introduced, and the mixture heated very gradually, the gas being collected by downward displacement in stoppered bottles, which must be placed in readiness, as the gas comes off very rapidly. A loose roll of dry filter paper in the neck of the retort will be useful to retain drops of liquid. These quantities will fill four pint bottles with the gas.

Fig. 174.—Preparation of hydriodic acid.

Hydriodic acid gas is very similar in its properties to hydrochloric and hydrobromic acids, fuming strongly in moist air, very readily absorbed by water, liquefied only under strong pressure, and solidified by extreme cold. It is much heavier, its specific gravity being 4·44. If a bottle of hydriodic acid gas be placed in contact with a bottle containing chlorine or bromine vapour diluted with air (fig. 133), it will be instantly decomposed, with separation of the beautiful violet vapour of iodine.

The aqueous solution of hydriodic acid is most conveniently prepared by passing hydrosulphuric acid gas through water in which iodine is suspended, $HS + I = HI + S$, the separated sulphur being filtered off, and the solution boiled to expel the excess of hydrosulphuric acid. Solution of hydriodic acid differs greatly from hydrochloric and hydrobromic acids, in being decomposed by exposure to air, its hydrogen being oxidised and iodine separated, which dissolves in the liquid and renders it brown.

This tendency of the hydrogen of hydriodic acid to combine with oxygen renders that acid a powerful *reducing* agent. It is even capable of converting hydrated sulphuric acid into hydrosulphuric acid—

$$HO.SO_3 + 4HI = HS + 4HO + I_4$$

so that when iodide of potassium is heated with concentrated sulphuric acid, hydrosulphuric acid is evolved in considerable quantity.

The action of hydriodic acid upon the metals and their oxides is generally similar to that of the other hydrogen acids.

When potassium is heated in a measured volume of hydriodic acid, the iodine is removed, and the hydrogen occupies half the original volume. Hence 1 volume of hydrogen is combined with 1 volume of iodine vapour in 2 volumes of hydriodic acid. One equivalent (47 grains) of potash is neutralised by 128 grains of hydriodic acid. This quantity occupies 4 volumes (8 grains O = 1 volume), so that 1 eq. or 4 volumes or 128 parts by weight of hydriodic acid, will contain 1 eq. or 2 volumes or 1 part by weight of hydrogen, and 1 eq. or 2 volumes or 127 parts by weight of *iodine vapour*.

Like chlorine and bromine, iodine is capable of displacing hydrogen from many organic compounds, and of taking its place, but its action in this respect is much feebler. The circumstance that the organic compounds containing iodine are generally much less volatile, and therefore more manageable than those of chlorine and bromine, leads to the extensive employment of this element in researches upon organic substances.

With olefiant gas, iodine forms a crystalline solid compound ($C_4H_4I_2$) corresponding to Dutch liquid (p. 86), and from this compound a yellow unstable aromatic liquid has been obtained, which is believed to be an *iodide of carbon*.

128. *Iodide of nitrogen.*—The action of chlorine, bromine, and iodine upon ammonia, exemplifies the difference in their attraction for hydrogen; for whilst chlorine and bromine, acting upon ammonia, cause the liberation of a certain amount of nitrogen, iodine simply removes two-thirds of the hydrogen, and itself fills up the vacancies thus occasioned, no nitrogen being liberated—

$$NH_3 + I_4 = NHI_2 + 2HI$$

the hydriodic acid thus formed combining with more ammonia to form hydriodate of ammonia.

To prepare the iodide of nitrogen, 20 grains of iodine are rubbed to powder in a mortar and mixed with half an ounce (measured) of strong ammonia; the mortar is covered with a glass plate, and after about half an hour the iodide of nitrogen is collected in separate portions upon four filters, which are allowed to drain and spread out to dry. The brown solution contains iodine dissolved in hydriodate of ammonia.

The iodide is a black powder, which explodes with a loud report even when touched with a feather, emitting fumes of hydriodic acid and purple vapour of iodine; its explosion is probably represented by the equation—

$$NHI_2 = N + HI + I$$

its violence being accounted for by the sudden evolution of a large volume of gas and vapour from a small volume of solid. Even when allowed to fall from the height of a few feet upon the surface of water, it explodes if perfectly dry. In the moist state it slowly undergoes decomposition.

129. Iodine forms two compounds with chlorine, the *protochloride of iodine* (ICl) and the *terchloride* (ICl_3). The former is a brown volatile liquid of irritating odour, obtained by distilling 1 part of iodine with 4 parts of chlorate of potash.

The terchloride forms fine red needle-like crystals, and is produced when iodine is acted upon with an excess of chlorine. *Bromides of iodine* have also been obtained, but their composition is not well known.

130. *Iodide of potassium.*—This salt is the most useful compound of iodine, being largely employed in medicine and in photography. It is generally prepared by decomposing iodide of iron with carbonate of potash.

The *iodide of iron* (also a useful medicine) is made by placing two parts of iodine in contact with one part of iron filings and ten parts of water. The iodine combines with part of the iron, evolving considerable heat, and producing the iodide of iron (FeI).

The liquid is decanted from the excess of iron, and one-third of the *weight of iodine* previously employed is dissolved in it. In this way, two-

of the iodide of iron are converted into sesqui-iodide (Fe_2I_3), so that ation contains a mixture of one equivalent of the iodide (FeI) and the sesqui-iodide (Fe_2I_3). It is now boiled, and carbonate of is gradually added as long as it causes a dark green precipitate of ic oxide of iron—

$$FeI + Fe_2I_3 + 4(KO.CO_2) = 4\,KI + FeO.Fe_2O_3 + 4CO_2$$

bonic acid is evolved with effervescence, and if the solution be and evaporated, it deposits beautiful cubical (or sometimes octa- crystals, which are generally milk-white and opaque, but occa- quite transparent. Pure iodide of potassium remains dry in y air, but if an excess of carbonate of potash is employed in its tion, the crystals retain some of that salt and become damp when l to air. The iodide of potassium dissolves easily in water and . If the solution be pure, it does not become coloured when mixed re hydrochloric acid; but if any iodate of potash be present in it, a sh colour will be produced, due to iodine liberated in the action iodic acid upon the hydriodic acid; $IO_5 + 5HI = I_5 + 5HO$. late of potash is liable to be present in those specimens which are d by dissolving iodine in potash, to obtain a mixture of iodide of um and iodate of potash (see p. 173), the latter salt being after- decomposed by heat.

FLUORINE.

The most ornamental mineral substance occurring in any abun- n this country is known as *fluor spar* or *Derbyshire spar* (fluoride um), and is found with several beautiful shades of colour—blue, violet, or green, and sometimes perfectly colourless, either in large , or in crystals, which have the form of a cube or of some solid l from it. The use of this mineral as a flux in smelting ores dates very remote period, and from this use the name fluor appears to een originally derived, but we have no record of its chemical ex- ion till about a century since, when Margraf found his glass retort ully corroded in distilling this mineral with sulphuric acid, and soon after announced that it contained lime and *fluoric acid;* but this chemist had fallen into the o which analysts are continually of mistaking products for educts, periments, as they were afterwards ed by Gay-Lussac and Thénard, particular consideration.

Fig. 175.

Hydrofluoric acid.—If powdered ar be mixed with twice its weight of vitriol, and heated in a leaden (fig. 175), the neck of which fits into a leaden condensing-tube, in a mixture of ice and salt, a colourless liquid distils over, and the in the retort is found to consist of sulphate of lime—

$$\underset{\text{Fluoride of calcium.}}{CaF} + HO.SO_3 = \underset{\text{Sulphate of lime.}}{CaO.SO_3} + \underset{\text{Hydrofluoric acid.}}{HF}.$$

lourless liquid (*hydrofluoric acid*) possesses most remarkable pro-

perties; it is powerfully acid, fumes strongly in the air, and has a most pungent irritating odour. If the air is at all warm the liquid begins to boil when taken out of the freezing mixture, and is soon entirely dissipated in vapour (boiling point, 60° F.) Should the operator have the misfortune to allow a drop to fall upon his hand, it will produce a very painful sore, even its vapour producing pain under the finger nails. Its attraction for water is so great, that the acid hisses like red-hot iron when brought in contact with it. But its most surprising property is that of rapidly corroding glass, which has already been alluded to as noticed by Margraf. Experiment soon proved that great analogy existed between the properties of this new acid and those of hydrochloric acid; and Ampère was led to institute a comparison between them, which caused him to adopt the opinion that the acid was a hydrogen acid, containing a new salt radical which he named fluorine; the name of the acid was then changed from fluoric to hydrofluoric acid.

This liquid has since been proved to be a solution of hydrofluoric acid in water, for if it be distilled with anhydrous phosphoric acid, which retains the water, it evolves hydrofluoric acid gas, which resembles hydrochloric acid gas in fuming strongly on contact with moist air, and being eagerly absorbed by water, but has a far more pungent odour. The perfectly dry gas has very little action upon glass.

It is remarkable that the solution of hydrofluoric acid, in its concentrated form, is not so heavy as a somewhat weaker acid. Thus, the acid of sp. gr. 1·06 acquires the sp. gr. 1·15 on addition of a little water, but on adding more water its sp. gr. is again reduced. It would hence appear that the acid of 1·15 is a definite hydrate of hydrofluoric acid; its composition corresponds to HF. 4HO. It distils unchanged at 248° F. The solution is generally kept in bottles made of gutta-percha.

The action of hydrofluoric acid upon metals and their oxides resembles that of hydrochloric acid. It dissolves all ordinary metals except gold, platinum, silver, mercury, and lead.

The property which renders this acid so useful to the chemist is its power of dissolving silica even in its most refractory form. When sand or flint reduced to powder is digested in a leaden or platinum vessel with hydrofluoric acid, it is gradually dissolved, and if the solution be evaporated, the whole of the silica will be found to have disappeared in the form of gaseous fluoride of silicon; $SiO_2 + 2HF = SiF_2 + 2HO$. If the silicic acid be combined with a base, the metal will be left as a fluoride, decomposable by sulphuric or hydrochloric acid. This renders hydrofluoric acid a most valuable agent in the analysis of the numerous mineral silicates which resist the action of other acids.

The corrosion of glass by hydrofluoric acid is now easily explained. Ordinary glass consists of silicate of soda or potash combined with silicate of lime or oxide of lead. The hydrofluoric acid attacks and removes the silica, and thus eats its way into the glass.

In order to demonstrate the action of this acid upon glass, a glass plate is warmed sufficiently to melt wax, a piece of which is then rubbed over it, until the glass is covered with a thin and pretty uniform coating. Upon this a word or drawing may be engraved with a sharp point so that the lines shall expose the glass. A mixture of powdered fluor spar with concentrated sulphuric acid is then poured over it, and allowed to remain for a quarter of an hour; the acid mixture is washed off, and the plate gently warmed to melt the wax, which may be wiped off with a little tow, when it will be found that the hydrofluoric acid evolved from the mixture has corroded those portions of the glass from which the graver had removed the wax. It

been attempted to apply this process to the production of engravings, but the leness of the plate has formed a very serious obstacle.
a leaden or platinum dish be at hand, it is better to place the glass to be etched the dish containing the mixture of fluor spar and sulphuric acid exposed to a gentle heat.

Many ingenious experiments have been made in order to obtain fluorine the separate state, but it was found that it invariably combined with e portion of the material of the vessel in which the operation was ducted. The most successful of the early attempts to isolate fluorine ears to have been made, at the suggestion of Davy, in a vessel of r spar itself, which could not, of course, be supposed to be in any way ted by it. A greenish gas was obtained, possessing chemical proper- similar to those of chlorine, but of much higher intensity. The diffi- y, however, of obtaining vessels of fluor spar adapted to these experi- its appears to have prevented any complete investigation of this most resting element.
The most recent experiments, in which fluoride of silver was decom- d by iodine, lead to the conclusion that fluorine is a colourless gas ch is without action upon dry glass or upon mercury, but they require nsion and confirmation.
he *composition of hydrofluoric acid* has been inferred from that of ide of calcium, which has been shown by analysis to contain one valent (20 parts by weight) of calcium combined with 19 parts by ht of fluorine. Assuming that hydrofluoric acid resembles hydro- ic acid in composition as well as in general character, and that 19 re- nts the equivalent of fluorine, this acid would contain 1 equivalent volumes) of hydrogen combined with 1 equivalent of fluorine, and be supposed that the 20 parts (1 equivalent) of hydrofluoric acid by 4 volumes (O = 1 volume), the hypothetical specific gravity of ofluoric acid gas would be 0·69, and that of fluorine 1·31.
lutions of the fluorides of potassium and the other alkali metals cor- glass slowly like hydrofluoric acid. These fluorides are capable of ining with the acid; thus fluoride of potassium forms KF. HF, which, dry, is a convenient source of hydrofluoric acid gas when moder- heated. The only fluoride possessed of much practical interest beside luoride of calcium is the mineral *kryolite* (κρυος, *frost*), which is a le fluoride of aluminum and sodium ($3NaF . Al_2F_3$) found abundantly reenland, and valuable as a source of aluminum and soda. The *topaz* ins fluorine, but in what form of combination is not well known; its constituents are alumina and silica.
uorides are also found, though in very small quantity, in sea water, hey have been discovered in plants and animals. Human bone con- about 2 per cent. of fluoride of calcium.
will be remembered that fluorine is the only element which is not n to form any compound with oxygen.

3. *Fluoride of silicon.*—If a mixture of powdered fluor spar and be heated, in a test-tube or small flask, with concentrated sulphuric a gas is evolved which has a very pungent odour, and produces thick fumes in contact with the air; it might at first be mistaken for fluoric acid, but if a glass rod or tube be moistened with water and ed to the gas, the wet surface becomes coated with a white film, proves, on examination, to be silicic acid. This result originated *elief that the gas consisted of fluoric* (now hydrofluoric) acid and

silica, but Davy corrected this view by showing that it really contai no oxygen, and consisted solely of silicon and fluorine. The gas is n called the fluoride of silicon, and represents silicic acid in which the oxy has been displaced by the fluorine; the change of places between these elements in the above experiment is represented by the subjoined e tion—

$$\underset{\text{Fluor spar.}}{2CaF} + \underset{\text{Silica.}}{SiO_2} + \underset{\text{Sulphuric acid.}}{2(HO.SO_3)} = \underset{\text{Sulphate of lime.}}{2(CaO.SO_3)} + \underset{\text{Fluoride of silicon.}}{SiF_2} + 2F$$

The formation of the crust of silica upon the wetted surface of the g is due to a decomposition which takes place between the fluoride of si and the water, in which the oxygen and fluorine again change places

$$SiF_2 + 2HO = SiO_2 + 2HF.$$

Since this latter equation shows that hydrofluoric acid is again for it would be expected that the glass beneath the deposit of silica woul found corroded by the acid; this, however, is not the case, and when experiment is repeated upon a somewhat larger scale, so that the w which has acted upon the gas may be examined, it will be found to in solution, not hydrofluoric acid, but an acid which does not act u glass, and is composed of hydrofluoric acid and fluoride of silicon; so the hydrofluoric acid produced when water acts upon the fluoride bines with a portion of the latter to produce the new acid (HF.S *hydrofluo-silicic acid.*

For the preparation of fluoride of silicon, 1 oz. of fluor spar and 1 oz. of pow glass are mixed together, and heated, in a Florence flask, with 7 oz. (measure oil of vitriol, the gas being collected in dry bottles by downward displacement fig. 160, p. 147). If a little of the gas be poured from one of the bottles into a filled up to the neck with water, the surface of the latter will become covered a layer of silica, so that if the flask be quickly inverted, the water will not pour it, and will seem to have been frozen. In a similar manner, a small tube with water and lowered into a bottle of the gas, will appear to have been f when withdrawn. A stalactite of silica some inches in length may be obtain allowing water to drip gently from a pointed tube into a bottle of the gas. Char written on glass with a wet brush are rendered opaque by pouring some flu of silicon upon them.

Fluoride of silicon is a substance of some importance in mineralo chemistry, since, by its aid, certain crystallised minerals may be s cially obtained under conditions which are not unlikely to have atte the production of the natural crystals. Thus, the mineral *staurotid staurolite* (σταυρός, *a cross*), or *granatite* or *cross-stone*, a naturally cry lised compound of alumina and silicic acid, may be obtained by the a of fluoride of silicon upon alternate layers of alumina and silica, heat whiteness in a porcelain tube. The fluoride of silicon, acting upon heated alumina, gives silicate of alumina and fluoride of aluminum—

$$3Al_2O_3 + 3SiF_2 = Al_2O_3.3SiO_2 + 2Al_2F_3$$

the newly-formed fluoride of aluminum, passing over a heated lay silica, produces more silicate of alumina, regenerating fluoride of silic

$$5SiO_2 + 2Al_2F_3 = 2(Al_2O_3.SiO_2) + 3SiF_2$$

that a given quantity of the fluoride of silicon will convert an indef antity of silica and alumina into the crystallised staurolite. It ap *bable* that other crystallised minerals have been formed in a si

ıer, by the action of minute quantities of such agents of transforma-
The frequent occurrence of minute quantities of fluorides in various
rals may thus have great significance.
ıe specific gravity of fluoride of silicon is 3·60. Assuming 0·93 to re-
nt the sp. gr. (weight of 1 vol.) of imaginary silicon vapour (see p. 165),
1·31 to represent the sp. gr. of fluorine, the number 3·55 would be the
of the weights of 1 vol. of silicon vapour and 2 vols. of fluorine ; so
2 vols. (1 eq.) of silicon vapour are combined with 4 vols. (2 eqs.)
ıorine, to form 2 vols. of fluoride of silicon.

4. *Hydrofluo-silicic acid* or *silico-fluoric acid.*—This acid is only
rn in the form of a solution, which is obtained by passing fluoride of
n into water—

$$3SiF_2 + 2HO = \underset{\text{Hydrofluo-silicic acid.}}{2(HF.SiF_2)} + SiO_2 .$$

gas must not be passed directly into the water, lest the separated
should stop the orifice of the tube, to prevent which, the latter
ld dip into a little mercury at the bottom of the water, when each
le, as it rises through the mercury into the water, will become sur-
ded with an envelope of gelatinous silica, and if the bubbles be very
ar, they may even form tubes of silica extending through the whole
ht of the water.

r preparing hydrofluo-silicic acid
l be found convenient to employ
ion stoneware bottle (fig. 176),
shed with a wide tube dipping
a cup of mercury placed at the
n of the water. 1 lb. of finely
ered fluor spar, 1 lb. of fine sand,
34 measured ounces of oil of vi-
are introduced into the bottle,
is gently heated upon a sand-
the gas being passed into about
ts of water. After 6 or 7 hours
water will have become pasty,
the separation of gelatinous
. It is poured upon a filter, and
the liquid has drained through
r as possible, the filter is wrung
cloth to extract the remainder
e acid solution, which will have
gr. of about 1·078.

Fig. 176.—Preparation of hydrofluo-silicic acid.

dilute solution of hydrofluo-
c acid may be concentrated
aporation up to a certain point, when it begins to decompose, evolving
s of fluoride of silicon, hydrofluoric acid remaining in solution and
ilising in its turn if the heat be continued. Of course the solution
des glass and porcelain when evaporated in them. If the solution of
ofluo-silicic acid be neutralised with potash, and stirred, a very cha-
ristic crystalline precipitate of silico-fluoride of potassium is formed—

$$HF.SiF_2 + KO = \underset{\substack{\text{Silico-fluoride}\\ \text{of potassium.}}}{KF.SiF_2} + HO .$$

it if an excess of potash be employed, a precipitate of gelatinous silica
be separated, fluoride of potassium remaining in the solution—

$$HF.SiF_2 + 3KO = 3KF + HO + SiO_2 .$$

One of the chief uses of hydrofluo-silicic acid is to separate the potash from its combination with certain acids, in order to obtain these in the separate state.

135. *Fluoride of boron* may be prepared by a process similar to that employed for fluoride of silicon, but it is also obtained by strongly heating a mixture of powdered anhydrous boracic acid with twice its weight of fluor spar in an iron tube—

$$3CaF + BO_3 = 3CaO + \underset{\text{Fluoride of boron.}}{BF_3}.$$

The fluoride of boron is a gas which fumes strongly in moist air like the fluoride of silicon. It is absorbed eagerly by water, with evolution of heat. One volume of water is capable of dissolving 700 volumes of fluoride of boron, producing a corrosive heavy liquid (sp. gr. 1·77) which fumes in air, and chars organic substances on account of its attraction for water. This solution is known as *fluoboric* or *borofluoric acid*, and its formation is explained by the equation—

$$BF_3 + 3HO = \underset{\text{Fluoboric acid.}}{BO_3.3HF}.$$

When the solution is heated, it evolves fluoride of boron until its specific gravity is reduced to 1·58, when it distils unchanged.

Hydrofluoboric acid is obtained in solution by adding a large quantity of water to fluoboric acid—

$$3(BO_3.3HF) = BO_3 + 6HO + \underset{\text{Hydrofluoboric acid.}}{3HF.2BF_3}.$$

This acid resembles the hydrofluo-silicic; its hydrogen may be exchanged for metals to form *borofluorides*.

136. *General review of chlorine, bromine, iodine, and fluorine.*—These four elements compose a natural group, the members of which are connected by the similarity of their chemical properties, far more closely than those of any other group of elements. They are usually styled the *halogens*, from their tendency to produce salts resembling sea-salt in their composition (ἅλς, *the sea*), and such salts are called *haloid salts*. These elements are also called *salt-radicals*, from their property of forming salts by direct union with the metals.

The equivalent weights of chlorine, bromine, iodine, and probably of fluorine, in the state of vapour, occupy the same volume as an equivalent of hydrogen, and each of these elements combines with an equal volume of hydrogen to form an acid which occupies the joint volumes of its constituents.

If one volume of hydrogen represents one atom, then the equivalent weights of these elements (occupying the same volume as hydrogen) will also represent their atomic weights, and they are decidedly mon-atomic elements.

The halogens also supply the most prominent example of the gradation in properties sometimes observed among the members of the same natural group of elements.

In the order of their chemical energy, that is, of the force with which they hold other elements in chemical combination with them, fluorine should stand first, its combining energy being so great as to cause a serious difficulty in isolating it at all; chlorine would rank next, then bromine, and iodine last.

Their equivalent weights follow the inverse order of their chemical energies: fluorine, 19; chlorine, 35·5; bromine, 80; iodine, 127;—numbers which, of course, also represent their relative specific gravities in the state of vapour.

A similar gradation is observed in the physical state and colour of those three which are well known; chlorine being a yellow gas, bromine a red liquid, boiling at 145° F., and iodine a black solid, boiling at 347° F.

Even in the exceptions which occur to the order of chemical energy above alluded to, the same progression is noticed; thus fluorine has so little attraction for oxygen that no oxide is known, chlorine has less attraction for oxygen than bromine (chloric acid being less stable than bromic), whilst bromine has less than iodine, which is said to be capable even of uniting directly with ozonised oxygen to form iodic acid.

The compounds of these elements with hydrogen are all gases distinguished by a powerful attraction for moisture and great similarity of odour.

Their potassium-salts all crystallise in the same (cubical) form.

The fluoride of silver is soluble in water; the chloride is insoluble in water, but dissolves very easily in ammonia; the bromide dissolves with some difficulty in ammonia; and the iodide is insoluble.

SULPHUR.

137. Sulphur is remarkable for its abundant occurrence in nature in the uncombined state, in many volcanic districts. It is also found, as sulphuretted hydrogen, in many mineral waters, and very abundantly in combination with metals, forming the numerous ores known as *sulphurets* or *sulphides*, of which the following are the most abundant:—

Iron pyrites,	Bisulphide of iron,	FeS_2
Copper pyrites,	Sulphide of iron and copper,	$Cu_2S . Fe_2S_3$
Galena,	Sulphide of lead,	PbS
Blende,	Sulphide of zinc,	ZnS
Crude antimony,	Sulphide of antimony,	SbS_3
Cinnabar,	Sulphide of mercury,	HgS.

Sulphur is plentifully distributed also, in combination with oxygen and a metal, in the form of *sulphates*, of which the most conspicuous are:—

Gypsum,	Sulphate of lime,	$CaO . SO_3 + 2HO$
Heavy spar,	Sulphate of baryta,	$BaO . SO_3$
Celestine,	Sulphate of strontia,	$SrO . SO_3$
Epsom salts,	Sulphate of magnesia,	$MgO . SO_3 + 7HO$
Glauber's salt,	Sulphate of soda,	$NaO . SO_3 + 10HO$.

In plants, sulphur is also found in the form of sulphates, and as a constituent of the vegetable albumen (of which it forms about 1·5 per cent.) present in the sap. It is also contained in certain of the essential oils remarkable for their peculiar pungent odour, such as—

Essence of garlic,	Sulphide of allyle,*	C_6H_5S
Essence of mustard,	Sulphocyanide of allyle,	$C_6H_5 . C_2NS_2$.

In animals, sulphur occurs as sulphates, as a constituent of albumen, fibrine, and caseine (in neither of which does it exceed 2 per cent.); and

* *Allium*, garlic.

in bile, one of the products from which (taurine, $C_4H_7NO_6S_2$) contains 25 per cent. of sulphur.

For our supplies of sulphur we are chiefly indebted to Sicily, where large quantities of it are found in an uncombined state in beds of blue clay. Magnificent crystalline masses of sulphate of strontia are often found associated with it; the sulphur itself sometimes occurs in the form of transparent yellow octahedra, but more frequently in opaque amorphous masses. The districts in which sulphur is found are usually volcanic, and those which border the Mediterranean are particularly rich in it. Sulphur has also been found in Iceland and California.

The *native* sulphur being commonly distributed in veins through masses of gypsum and celestine, has to be separated from these by the action of heat. When the ores contain more than 12 per cent. of sulphur, the bulk of it is melted out, the ore being thrown into rough furnaces or cauldrons with a little fuel, and smothered up with earth, so as to prevent the com-

Fig. 177.—Distillation of sulphur.

bustion of the sulphur, which runs down in the liquid state to the bottom of the cauldron, and is drawn out into wooden moulds. But when the proportion of sulphur is small, the ore is heated so as to convert the sulphur into vapour, which is condensed in another vessel. The operation is conducted in Sicily in rows of earthen jars (A, fig. 177), heated in a long furnace,

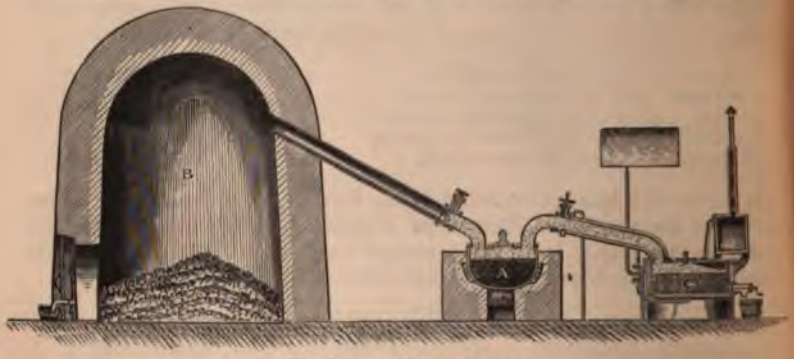


Fig. 178.—Sulphur refinery.

and provided with short lateral pipes, which convey the sulphur into similar jars (B) standing outside the furnace, in which the vapour of sulphur condenses in the liquid state, and flows out into pails of water. The

sulphur obtained by this process is imported as *rough sulphur*, and contains 3 or 4 per cent. of earthy impurities. In order to separate these it is redistilled, in this country, in an iron retort (A, fig. 178), from which the vapour is conducted into a large brick chamber (B), upon the sides of which it is deposited in the form of a pale yellow powder (*flowers of sulphur*, or *sublimed sulphur*). When the operation has been continued for some time the walls of the chamber become sufficiently hot to melt the sulphur, which is allowed to collect, and afterwards cast in wooden moulds, forming *roll sulphur* or *brimstone*. *Distilled sulphur* is obtained by allowing the vapour to pass from the retort into a small receiving-vessel (C) cooled by water, where it condenses in the liquid state; this variety of sulphur is preferred for the manufacture of gunpowder, for reasons which will be stated hereafter.

Sulphur is readily distilled on a small scale in a Florence flask (fig. 179), another flask cut off at the neck (see p. 166) being employed as a receiver. The flask containing the sulphur should be supported upon a thin iron wire triangle, and heated by a gauze-burner, at first gently, and afterwards to the full heat. Flowers of sulphur will at first condense in the receiver, and will be followed by distilled sulphur when the temperature increases. A slight explosion of the mixture of sulphur vapour and air may take place at the commencement of the distillation. An ounce of sulphur may be distilled in a few minutes.

Fig. 179.—Distillation of sulphur.

We are by no means entirely dependent upon Sicily for sulphur, for this element can be easily extracted from iron and copper pyrites, both which are found abundantly in this country.

Iron pyrites forms the yellow metallic-looking substance which is often met with in masses of coal, sometimes in distinct cubical crystals, and which is to be picked up in large quantities on some sea-beaches, where it occurs in rounded nodules, rusty outside, but having a fine radiated metallic fracture. When this mineral is strongly heated it gives up part of its sulphur; at a very high temperature one half of the sulphur may be separated—

$$FeS_2 = FeS + S$$

but by an ordinary furnace heat only about one-fourth can be obtained. The distillation of iron pyrites is sometimes effected in conical fire-clay vessels (fig. 180) closed at the wider end, and stopped towards the other with a perforated plate to allow the passage of the sulphur vapour. Each vessel contains 100 lbs. of pyrites, and yields 14 lbs. *of sulphur.*

Fig. 180.—Furnace for distillation of sulphur from pyrites.

The sulphur obtained in this way has a green colour, due to the presence of a little sulphide of iron carried over mechanically during the distillation; in order to purify it, it is melted and allowed to cool slowly, when the sulphide of iron subsides; the upper portion of the mass is then further purified by distillation.

Sulphur may also be obtained from copper pyrites ($Cu_2S \cdot Fe_2S_3$) in the process of roasting the ore previously to the extraction of the copper. The ore is heaped up into a pyramid, the base of which is about 30 feet square; a layer of powdered ore is placed at the bottom to prevent too rapid access of air; above this there is a layer of brushwood; a wooden chimney is placed in the centre, and is made to communicate with air-passages left between the faggots; around this chimney the large fragments of the ore are piled to a height of about 8 feet, and a layer of powdered ore, about 12 inches deep, is strewn over the whole. The heap contains about 2000 tons of pyrites, and will yield 20 tons of sulphur. The fire, being kindled by dropping lighted faggots down the chimney, burns very slowly because of the limited access of air, and after a few days sulphur is seen to exude from the surface, and is received in cavities made for the purpose in different parts of the heap; the roasting requires five or six months for its completion. In this operation a part of the sulphur has been separated by the mere action of heat, and another part has been displaced by the oxygen of the air, which has converted a portion of the iron into an oxide; a part of the separated sulphur has been burnt, the rest having escaped combustion on account of the limited access of air.

The sulphur extracted from pyrites is generally found to contain a little arsenic, which is frequently associated with those minerals. Immense quantities of sulphur are consumed in this country for the manufacture of sulphuric acid, gunpowder, lucifer matches, vulcanised caoutchouc, and for making the sulphurous acid employed in bleaching processes.

138. *Properties of sulphur.*—In its ordinary forms sulphur has a characteristic yellow colour, though *milk of sulphur*, or precipitated sulphur (obtained by adding an acid to the solution of sulphur in an alkali), is white. It suffers electrical disturbance with remarkable facility, so that when powdered in a dry mortar it clings to it with great pertinacity.

One of the most remarkable features of sulphur is its inflammability, due to its tendency to combine with oxygen at a moderately elevated temperature. It melts at a heat not much above the boiling point of water (239° F.), and inflames at about 500° F., burning with a pale blue flame, and emitting the well-known suffocating odour of sulphurous acid (SO_2).

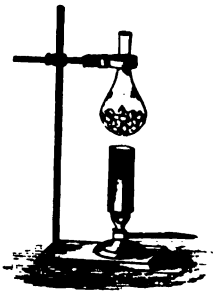


Fig. 181.

The changes in the physical condition of this element under the influence of heat are very extraordinary. If a quantity of sulphur be introduced into a Florence flask and subjected to a gradually increasing heat (fig. 181), it is soon converted into a pale yellow limpid liquid (250° F.), the colour of which becomes gradually brown as the heat rises, until, at about 350° F., it is nearly black and opaque, and is so viscid that the flask may be inverted without spilling it; at this point the temperature of the sulphur remains stationary for a time, notwithstand-

ing that it is still over the flame, showing that heat is becoming latent in converting the sulphur into the new modification. On continuing the heat, the sulphur once more becomes liquid (500°), though not so mobile as at first, and at a much higher temperature (836° F.) it boils, and is converted into a brownish red very heavy vapour; at this point of the experiment, an explosion of the mixture of sulphur vapour with air often takes place. The flask may now be removed from the flame, and a little of the sulphur poured into a vessel of water, through which it will descend in a continuous stream, forming a soft elastic string like india-rubber; the portion remaining in the flask will be observed, as it cools, to pass again through the same states, becoming viscid at 350° and very liquid at 250°; another portion may now be poured into water, through which it will fall in isolated drops, solidifying into yellow brittle crystalline buttons of ordinary sulphur. As the portion of sulphur left in the flask cools, it will be found to deposit small tufts of crystals, and ultimately to solidify altogether to a yellow crystalline mass.

The brown *ductile sulphur*, when kept for a few hours, will become yellow and brittle, passing, in great measure, spontaneously into the crystalline sulphur. The change is accelerated by a gentle heat, and is attended with evolution of the heat which the sulphur was found to absorb at 350° F. Both these varieties of sulphur are, of course, insoluble in water, and they are not dissolved to any great extent by alcohol and ether. If the crystalline variety be shaken with a little bisulphide of carbon it rapidly dissolves, and on allowing the solution to evaporate spontaneously, it deposits beautiful octahedral crystals, resembling those of native sulphur (fig. 182). Ductile sulphur, however, is insoluble in bisulphide of carbon.

When flowers of sulphur are shaken with bisulphide of carbon, a considerable quantity passes into solution, the remainder consisting of the *amorphous*, or insoluble sulphur. Roll sulphur dissolves to a greater extent, and sometimes entirely, in the bisulphide, and distilled sulphur is always easily soluble.

The soluble and insoluble forms of sulphur appear to represent distinct chemical varieties of the element. When a solution of sulphuretted hydrogen (HS) is decomposed by the galvanic battery, the hydrogen, as would be expected, is separated at the negative pole, and the sulphur at the positive pole (p. 21). The sulphur, therefore, was the *electronegative* element of the compound. This sulphur is soluble in bisulphide of carbon. When an acid is added to a solution of an alkaline sulphide containing more than one equivalent of sulphur, the excess of the latter is precipitated, and is then also found to be soluble in bisulphide of carbon, for it played an electronegative part towards the metal with which it was in combination.

When sulphurous acid (SO_2) is decomposed by the battery, the sulphur is separated at the negative pole, showing that it played an *electropositive* part in the sulphurous acid. This electropositive sulphur is insoluble in bisulphide of carbon. The sulphur in the chloride of sulphur (S_2Cl) also plays an electropositive part, and accordingly, when this compound is decomposed by water, the sulphur which separates is insoluble in bisulphide of carbon. The existence of these two forms of sulphur affords some support to the theory of the dual constitution of the elements noticed at p. 51.

The electropositive sulphur would be expected to manifest a greater attraction for oxygen than the electronegative variety, and accordingly, it

is found to be far more easily oxidised by nitric acid. Electropositive or insoluble sulphur is converted into electronegative or soluble sulphur by the action of a moderate heat, itself evolving heat during the process of conversion. When melted in contact with sulphurous acid, the soluble sulphur is converted externally into the insoluble form.

Fig. 182.

Crystalline or soluble sulphur is capable of existing in two distinct forms. The natural form of crystallised sulphur is the octahedron with a rhombic base (fig. 182), and this is the usual form which sulphur assumes when crystallised from its solutions. But if sulphur be melted in a covered crucible, allowed to cool until the surface has congealed, and the remaining liquid portion poured out after piercing the crust (with two holes, one for admission of air), the crucible will be lined with beautiful needles which are oblique prisms (fig. 183). These crystals are brownish yellow, and transparent when freshly made; but they soon become opaque yellow, and although they retain their prismatic appearance, they have now changed into minute rhombic octahedra, the change being attended with evolution of heat. On the other hand, if a crystal of octahedral sulphur be exposed for a short time to a temperature of about 230° F. (in a boiling saturated solution of common salt, for example), it becomes opaque, in consequence of the formation of a number of minute prismatic crystals in the mass.

Fig. 183.

The difference between these two forms of crystalline sulphur extends to their fusing-points and specific gravities; the prismatic sulphur fusing at 248° F., and the octahedral sulphur at 239° F.; the specific gravity of the prisms being 1·98, and that of the octahedra 2·05.

Roll sulphur, when freshly made, consists of a mass of oblique prismatic crystals, but after being kept for some time, it consists of octahedra, although the mass generally retains the specific gravity proper to the prismatic form. This change in the structure of the mass, taking place when its solid condition prevented the free movement of the particles, gives rise to a state of tension which may account for the extreme brittleness of roll sulphur. If a stick of sulphur be held in the warm hand, it often splits, from unequal expansion. These peculiarities of sulphur deserve careful study, as helping to elucidate the spontaneous alterations in the structure of glass, iron, &c., under certain conditions.

Flowers of sulphur do not present a crystalline structure, but consist of spherical granules composed of insoluble sulphur enclosing soluble sulphur. Hot oil of turpentine dissolves sulphur freely, and when the solution is allowed to stand, the crystals which are deposited whilst the solution is hot have the prismatic form, but as it cools, octahedra are separated.

The following table exhibits the chief *allotropic* forms of sulphur:—

	Sp. gr.	Fusing point.	
Octahedral Electro negative	2·05	239°	Soluble in bisulphide of carbon.
Prismatic	1·98	248°	Soluble in bisulphide of carbon.
Ductile Amorphous *Electropositive*	1·96	Becomes octahedral.	Insoluble in bisulphide of carbon.

octahedral is by far the most stable of the three, and is the ultimate ion which the others assume.

er varieties of sulphur, such as a black and a red modification, have escribed, but they are of minor importance.

hur is capable of entering into direct combination with several other ts. It unites with chlorine and with some of the metals, if finely d, even at the ordinary temperature, and it is capable of combining gh temperature with all the non-metals except nitrogen, and with all the metals.

nixture of 2 parts of copper filings and 1 part of sulphur, or of equal weights of ngs and sulphur, be heated in a Florence flask or a test-tube, the combination attended with vivid combustion.

so-called *Lemery's volcano* was made by mixing iron filings with two-thirds of eight of powdered sulphur, and burying several pounds of the moist mixture earth, when the heat evolved by the rusting of part of the iron provoked the ic combination of the remainder with the sulphur, and the consequent develop- f much steam.*

ral metals may be made to burn in sulphur vapour, as in oxygen, by heating phur in a Florence flask with a gauze burner, so keep the flask constantly filled with the brown Potassium and sodium, introduced in deflagrat- ons, take fire spontaneously in the vapour (fig.

Fig. 184.

il of copper wire glows vividly in sulphur vapour, comes converted into a brittle mass of sulphide of

phur dissolves, though slowly, in boiling itrated nitric and sulphuric acids, being ed by the former into sulphuric, and by tter into sulphurous acid. It is far more y converted into sulphuric acid by a mix- f nitric acid and chlorate of potash. The s dissolve sulphur when heated, yielding or red solutions which contain hyposulphites of the alkalies and des of their metals.

re is a very general resemblance in composition between the com- s of sulphur and those of oxygen with the same elements.

Hydrosulphuric Acid.

. *Sulphuretted hydrogen*, or hydrosulphuric acid, has been already oned as occurring in some mineral waters, as at Harrowgate. It is und in the gases emanating from volcanoes, sometimes amounting -fourth of their volume. It is a product of the putrefaction of c substances containing sulphur, and is one of the causes of the ing smell of drains, &c. Eggs, which contain a considerable pro- n of sulphur, evolve sulphuretted hydrogen as soon as they begin nge, and hence the association between this gas and the "smell of eggs." The same smell is observed when a kettle boils over upon or coal fire, the hydrogen liberated from the water combining with lphur present in the fuel.

nixture of 60 parts of fine iron filings, 2 of sal-ammoniac, and 1 of sulphur, made paste with water, is very useful for making the joints of iron tubes air-tight, for *nto a hard cement, the iron combining* with the sulphur.

Hydrosulphuric acid is also found among the products of destructive distillation of organic substances containing sulphur; it was mentioned among the products from coal, in which it is for the most part combined with the ammonia formed at the same time, producing hydrosulphate of ammonia.

It may be produced, though not in large quantity, by the direct union of hydrogen with sulphur vapour at a high temperature, or by passing a mixture of sulphur vapour and steam through a tube filled with red-hot pumice stone (the latter encouraging the action by its porosity). Hydrosulphuric acid is more readily formed by heating a damp mixture of sulphur and wood charcoal, and may be obtained in large quantity by heating a mixture of equal weights of sulphur and tallow, the latter furnishing the hydrogen.

Preparation of hydrosulphuric acid.—For use in the laboratory, where it is very largely employed in testing for and separating metals, hydrosulphuric acid is generally prepared by decomposing sulphide of iron with diluted sulphuric acid—

$$\underset{\text{Sulphide of iron.}}{FeS} + HO.SO_3 = \underset{\text{Hydrosulphuric acid.}}{HS} + \underset{\text{Sulphate of iron.}}{FeO.SO_3}.$$

To obtain sulphide of iron, a mixture of 3 parts of iron filings with 2 parts of flowers of sulphur is thrown, by small portions at a time, into an earthen crucible (A, fig. 185), heated to redness in a charcoal fire, the crucible being covered after each portion has been added. The iron and sulphur combine with combustion, and when the whole of the mixture has been introduced, the crucible is allowed to cool, the mass of sulphide of iron broken out, and a few fragments of it are introduced into a bottle (fig. 186) provided with a funnel tube for the addition of the acid, and a bent tube for conducting the gas through a small quantity of water, to remove any splashes of sulphate of iron. From the second bottle the gas is conducted by a glass tube with a caoutchouc joint, either down into a gas-bottle, or into water, or any other liquid upon which the gas is intended to act. The fragments of sulphide of iron should be covered with enough water to fill the gas-bottle to about one-third, and strong sulphuric acid added by degrees through the funnel, the bottle being shaken, until effervescence is observed. An excess of strong sulphuric acid stops the evolution of gas by precipitating a quantity of white anhydrous sulphate of iron, which coats the sulphide and defends it from the action of the acid. When no more gas is required, the acid liquid should be at once poured away, leaving the fragments of sulphide of iron at the bottom of the bottle for a fresh operation. The liquid, if set aside, will deposit beautiful green crystals of *copperas* or sulphate of iron ($FeO.SO_3 + 7HO$).

Fig. 185.

Fig. 186.—Preparation of hydrosulphuric acid.

Since the sulphide of iron prepared as above generally contains a little metallic

on, the sulphuretted hydrogen is mixed with free hydrogen, which does not gene-lly interfere with its uses. The pure gas may be prepared by heating sulphide of timony (crude antimony) in a flask with hydrochloric acid—

$$SbS_3 + 3HCl = 3HS + SbCl_3 .$$

Properties of hydrosulphuric acid.—This gas is at once distinguished om all others by its disgusting odour. It is one-fifth heavier than air p. gr. 1·1912). Its gaseous state is not permanent, but a pressure of 17 tmospheres is required to reduce it to a colourless liquid, which congeals a transparent solid at $-122°$ F. Water absorbs about three times its olume of sulphuretted hydrogen at the ordinary temperature; both the as and its solution are feebly acid to red litmus paper. The gas is very ombustible, burning with a blue flame like that of sulphur, and yielding, s the chief products, water and sulphurous acid—

$$HS + O_3 = HO + SO_2$$

little hydrated sulphuric acid ($HO . SO_3$) is also formed, and unless the upply of air is very good, some of the sulphur will be separated; thus, if taper be applied to a bottle filled with sulphuretted hydrogen, a good deal of sulphur will be deposited upon the sides. This combustibility of sulphuretted hydrogen is of the greatest importance in those processes of chemical manufacture in which this gas is evolved (as in the preparation of ammoniacal salts from gas liquors), enabling it to be disposed of in the furnace instead of becoming a nuisance to the neighbourhood. The gas causes fainting when inhaled in large quantity, and appears much to de-press the vital energy when breathed for any length of time even in a diluted state.

When dissolved in water, hydrosulphuric acid is slowly acted upon by the oxygen of the air, which converts its hydrogen into water, and causes a white deposit of (electronegative or soluble) sulphur.

This is a great drawback to the use of this indispensable chemical in the labor-atory, since the solution of hydrosulphuric acid is so soon rendered useless. To diminish it as far as possible, the solution should be made either with boiled water (free from dissolved air), or with water which has already been once charged with the gas and spoilt by keeping, for all the oxygen dissolved in this water will have been con-sumed by the former portion of gas. The gas should be passed through the water until, on closing the bottle with the hand and shaking violently, the pressure is found to act outwards, showing the water to be saturated with the gas. By closing the bottle with a greased stopper, and inverting it, the solution may be preserved for some weeks, even though occasionally opened for use.

In preparing the solution of hydrosulphuric acid, a certain quantity of the gas always escapes absorption. To prevent this from becoming a nuisance, the bottle containing the water to be charged with gas may be covered with an air-tight caoutchouc cap having two tubes, through one of which passes the glass tube con-veying the gas down into the water, and through the other, a tube conducting the excess of gas either into a gas-burner, where it may be consumed, or into a solution of ammonia which will absorb it, forming the very useful hydrosulphate of am-monia.

The hydrogen of the hydrosulphuric acid is oxidised immediately by nitrous acid (NO_3), the sulphur being separated, and a considerable quan-tity of nitrite of ammonia produced—

$$NO_3 + 6HS = NH_3 + 3HO + S_6 .$$

Concentrated nitric acid also oxidises the hydrogen and a part of the sulphur, sulphate of ammonia ($NH_3 . HO . SO_3$) being found in the solu-tion, and a pasty mass of sulphur separated. Chlorine, bromine, and iodine *at once appropriate its hydrogen* and separate the sulphur.

In its action upon the metals and their oxides, hydrosulphuric acid resembles hydrochloric and the other hydrogen acids. Many of the metals displace the hydrogen and form metallic sulphides. This usually requires the assistance of heat, but mercury and silver act upon the gas at the ordinary temperature. Thus, if sulphuretted hydrogen be collected over mercury, the surface of the latter becomes coated with a black film of sub-sulphide of mercury; $HS + Hg_2 = H + Hg_2S$. In a similar way the surface of silver is slowly tarnished when exposed to sulphuretted hydrogen, its surface being covered with a black film of sulphide of silver. It is on this account that silver plate is so easily blackened by the air of towns, which is contaminated with sulphuretted hydrogen. An egg spoon is always blackened by the sulphur from the egg. Silver coins kept in the pocket with lucifer matches are blackened, from the formation of a little sulphide of silver. The original brightness of the coin may be restored by rubbing it with a solution of cyanide of potassium, which dissolves the sulphide of silver.

When heated in the gas, several metals displace the hydrogen from it. Thus, potassium acts upon it in a corresponding manner to that in which it acts upon water—

$$\begin{array}{lllllll} 2HO & + & K & = & KO.HO & + & H \\ 2HS & + & K & = & KS.HS & + & H \end{array}$$

forming *hydrosulphate of* (*sulphide of*) *potassium* (KS. HS).

Tin removes the whole of the sulphur from hydrosulphuric acid at a moderate heat; $Sn + HS = H + SnS$.

When hydrosulphuric acid acts upon a metallic oxide, it generally converts it into a sulphide corresponding to the oxide, whilst the hydrogen and oxygen unite to form water. Oxide of lead in contact with the gas yields black sulphide of lead and water; $PbO + HS = PbS + HO$. Even if the oxide of lead be combined with an acid, the same change is produced by hydrosulphuric acid; and hence paper impregnated with a salt of lead is used as a test for the presence of this gas. Thus, if paper be spotted with a solution of nitrate (or acetate) of lead, it will indicate the presence of even minute quantities of sulphuretted hydrogen (in impure coal-gas, for example) by the brown colour imparted to the spots, the nitrate of lead being decomposed by the hydrosulphuric acid—

$$\underset{\text{Nitrate of lead.}}{PbO.NO_5} + HS = \underset{\text{Nitric acid.}}{HO.NO_5} + PbS.$$

It is in this manner that paints containing white lead (carbonate of lead) are darkened by exposure to the air of towns. Cards glazed with white lead, and engravings on paper whitened with that substance, suffer a similar change. Paintings, whether in oil or water colours, in which lead is an ingredient, are also injured by air containing sulphuretted hydrogen. The interesting observation has recently been made that such colours, damaged by the formation of sulphide of lead, are restored by the continued action of light and air, the black sulphide of lead becoming oxidised and converted into the white sulphate of lead—

$$PbS + O_4 = PbO.SO_3.$$

In the dark this restoration does not take place, so that it is often a mistake to screen pictures from the light by a curtain.

In cases where the sulphide corresponding to the oxide is of an unstable

cter, the action of hydrosulphuric acid upon the oxide will be attended separation of sulphur. This is the case with peroxide of iron—

$$Fe_2O_3 + 3HS = 2FeS + 3HO + S$$

seen in the purifiers in which that substance is employed for removhe sulphuretted hydrogen from coal-gas.

e action of hydrosulphuric acid upon the chlorides and other haloid of the metals generally resembles its action upon the oxides of the metals.

ost of the sulphides of the metals, like the corresponding oxides, are uble in water, but many of the sulphides are also insoluble in diluted and in alkalies, so that when hydrosulphuric acid is brought into ct with the solutions of metals, it will often precipitate the metal in orm of a sulphide having some characteristic colour or other property hich the metal may be identified.

y solution of lead will give a *black* precipitate with solution of hydrosulphuric the sulphide of lead being insoluble in diluted acids and in alkalies.

olution of antimony (tartar-emetic, for example, the tartrate of antimony and h) mixed with an excess of hydrochloric acid, gives an *orange*-coloured preci- (Sb_2S_3) on adding hydrosulphuric acid; but if another portion be mixed with cess of potash before adding the hydrosulphuric acid, there will be no precipifor the sulphide of antimony is soluble in alkalies.

loride of cadmium gives a brilliant *yellow* precipitate of sulphide of cadmium ding hydrosulphuric acid.

lphate of zinc yields a *white* precipitate of sulphide of zinc (ZnS), but if a little chloric acid be previously added, no precipitate is formed, the sulphide of zinc soluble in acids. On neutralising the hydrochloric acid with ammonia, the ide of zinc is at once precipitated.

is evident that, in a solution containing cadmium and zinc, the metals may be ated by acidifying the liquid with hydrochloric acid, and adding excess of sulphuric acid, which precipitates the sulphide of cadmium only. On filtering olution, and adding ammonia, the sulphide of zinc is precipitated.

lphur-acids and *sulphur-bases*.—Those sulphides which are soluble e alkalies are often designated sulphur-acids, whilst the sulphides of lkali-metals are sulphur-bases. These two classes of sulphides comto form *sulphur-salts* analogous in composition to the oxygen-salts of ame metals. Thus, there have been crystallised, the salts

Sulphostannate of	(sulphide of)	sodium,	$2NaS.SnS_2$
Sulphantimoniate	,,	,,	$3NaS.SbS_5$
Sulpharseniate	,,	,,	$3NaS.AsS_5$

e sulphostannic (SnS_2), sulphantimonic (SbS_5), and sulpharsenic $_5$) acids respectively, corresponding to stannic (SnO_2), antimonic $_5$), and arsenic (AsO_5) acids.

e *action of air upon the sulphides* of the metals is often turned to nt in chemical manufactures. At the ordinary temperature, the sules of those metals which form alkaline oxides (such as sodium and m), when exposed to the air in the presence of water, yield, first, ures of the oxide and bisulphide, $2NaS + O = NaO + NaS_2$; and wards the hyposulphite, $NaS_2 + O_3 = NaO.S_2O_2$. This change is times turned to account for the manufacture of hyposulphite of

When the metal forms a less powerful base with oxygen, the sul- is often converted into sulphate by exposure to moist air; thus, $+ O_4 = CuO.SO_3$, which is taken advantage of for the separation *pper from tin ores.*

The black sulphide of iron (FeS), when exposed to moist air, becomes converted into red peroxide of iron, with separation of sulphur—

$$2FeS + O_3 = Fe_2O_3 + S_2$$

a change which enables the gas manufacturer to revive, by the action of air, the peroxide of iron employed for removing the sulphuretted hydrogen from coal-gas (see p. 193).

When *roasted* in air at a high temperature, the sulphides corresponding to the more powerful bases are converted into sulphates; thus $ZnS + O_4 = ZnO.SO_3$, which explains the production of sulphate of zinc by roasting blende. But in most cases part of the sulphur is converted into sulphurous acid at the same time. Subsulphide of copper, for instance, is partly converted into oxide of copper by roasting, $Cu_2S + O_4 = 2CuO + SO_2$, a change of great importance in the extraction of copper from its ores.

140. *Composition of hydrosulphuric acid.*—When this acid acts upon a metallic oxide, the oxide, as a general rule, is found to exchange 8 parts by weight of oxygen for 16 parts of sulphur; therefore, if 8 be taken as the equivalent of oxygen (H = 1), 16 will represent that of sulphur, and the equivalent weight of hydrosulphuric acid will be 17 (containing 1 eq. of hydrogen and 1 eq. of sulphur). If metallic tin be heated in a measured volume of hydrosulphuric acid gas, it removes the whole of the sulphur, whilst the hydrogen which is left occupies the same volume as the original hydrosulphuric acid. Hence, 1 vol. of this gas contains 1 vol. of hydrogen.

The weight of 1 vol. (sp. gr.) of HS . .	=	1·1912
Deducting the weight of 1 vol. (sp. gr.) of H	=	0·0692
There remains		1·1220

for the weight of the sulphur vapour contained in 1 vol. of hydrosulphuric acid. The specific gravity (or weight of 1 vol.) of sulphur vapour (at 1900° F.) is 2·23, so that the weight of sulphur vapour in 1 vol. of hydrosulphuric acid represents half a volume; accordingly, there are, in 1 vol. of HS, 1 vol. of hydrogen and ½ vol. of sulphur vapour. But 1 eq. (17 parts by weight) of hydrosulphuric acid occupies 2 vols. (8 parts of oxygen representing 1 vol.), and would contain 1 eq. of hydrogen (occupying 2 vols.) and 1 eq. of sulphur (occupying 1 vol.).

The composition of hydrosulphuric acid by volume, therefore, is precisely similar to that of water, and its molecular formula (1 vol. = 1 atom of H) would be H_2S (= 2 vols.), the atomic weight of sulphur being 32, and occupying, in the state of vapour at 1900° F., the same volume as 1 part by weight of hydrogen.

141. *Influence of temperature upon the specific gravity of gases and vapours.*—The specific gravity of a gas or vapour being defined as its weight, compared with that of an equal volume of dry and pure air at the same temperature and pressure, it might be supposed that so long as the temperatures were equal, their actual thermometric value would not influence the specific gravity. Indeed, with those gases and vapours which are condensible with difficulty, this is actually the case. Thus, if equal volumes of oxygen and air be weighed, either at a low or a high temperature, provided their temperatures are the same, their weights will always *stand to* each other in the ratio of 1·1057 : 1 .

But with many vapours it is found that if they be weighed at temperatures too nearly approaching to their condensing points, their specific gravities are much higher than they are found to be at higher temperatures. Sulphur affords a very well-marked instance of this. It boils at 836° F., and if its vapour be weighed at a temperature of 900° F., it is found to weigh 6·617 times as much as an equal volume of air at 900° F., so that its specific gravity would be 6·617, or 1 eq. of sulphur would occupy $\frac{1}{3}$ vol. (O = 1 vol.). But if the vapour of sulphur be weighed at 1900° F., it is found to weigh only 2·23 times as much as an equal volume of air at the same temperature and pressure, so that its specific gravity is only one-third of that formerly given, and 1 eqt. of sulphur occupies 1 vol.

142. *Persulphide of hydrogen.*—The composition of this substance is not yet satisfactorily ascertained. The similarity of its chemical properties to those of binoxide of hydrogen prompts the wish that its formula may be HS_2. Some analyses, however, seem to lead to the formula HS_3, but since the persulphide is a liquid capable of dissolving free sulphur, which is not easily separated from it, there is much difficulty in determining the exact proportion of this element with which the hydrogen is combined.

When equal weights of slaked lime and sulphur are boiled with water, an orange-coloured liquid is formed, which contains hyposulphite of lime, bisulphide of calcium, and pentasulphide of calcium (CaS_5)—

$$3CaO + S_6 = \underset{\text{Hyposulphite of lime.}}{CaO.S_2O_2} + \underset{\text{Bisulphide of calcium.}}{2CaS_2}.$$

When hydrochloric acid is added to the filtered solution, an abundant precipitation of sulphur occurs, and much hydrosulphuric acid is evolved—

$$CaS_2 + HCl = CaCl + HS + S.$$

But if the solution be poured by degrees into a slightly warm mixture of hydrochloric acid with twice its bulk of water, and constantly stirred, a yellow heavy oily liquid collects at the bottom, which is the persulphide of hydrogen—

$$CaS_2 + HCl = HS_2(?) + CaCl.$$

The acid having been kept in excess, the persulphide has been preserved from the decomposition which it suffered in the presence of the alkaline solution in the former experiment. For the persulphide of hydrogen very closely resembles the binoxide in the facility with which it may be decomposed into hydrosulphuric acid and sulphur; it undergoes spontaneous decomposition even in sealed tubes, and the hydrosulphuric acid then becomes liquefied by its own pressure. Most of the substances, the contact of which promotes the decomposition of the binoxide of hydrogen, have the same effect upon the persulphide. This compound has a peculiar odour which appears to affect the eyes; of course, its vapour is mixed with that of hydrosulphuric acid.

Oxides of Sulphur.

143. Only two compounds of sulphur with oxygen have been obtained in the separate state, viz., *sulphurous acid* (SO_2) and *sulphuric acid* (SO_3). Four more have been obtained in combination with water, viz., *dithionic* (*θεῖον, sulphur*) or *hyposulphuric* (S_2O_5), *trithionic* (S_3O_5), *tetrathionic* (S_4O_5), and *pentathionic* (S_5O_5) acids. One of the oxides has only been obtained in the form of salts, viz., *hyposulphurous* acid (S_2O_2).

The following table exhibits their composition, the imaginary oxides being distinguished by (?) :—

Oxides of Sulphur.

Name.	Equivalent Formula.	By Weight.	
		Sulphur.	Oxygen.
Hyposulphurous acid, . . ?	S_2O_2	32	16
Sulphurous ,, . .	SO_2	16	16
Sulphuric ,, . .	SO_3	16	24
Dithionic ,, . . ?	S_2O_5	32	40
Trithionic ,, . . ?	S_3O_5	48	40
Tetrathionic ,, . . ?	S_4O_5	64	40
Pentathionic ,, . . ?	S_5O_5	80	40

Sulphurous Acid.

144. In nature, sulphurous acid is but rarely met with; it exists in the gases issuing from volcanoes. Although constantly discharged into the air of towns by the combustion of coal (containing sulphur), it is so easily oxidised and converted into sulphuric acid, that no considerable quantity is ever found in the atmosphere. Sulphurous acid has been already mentioned as the sole product of the combustion of sulphur in dry air and oxygen, but it is generally prepared for chemical purposes by removing part of the oxygen from sulphuric acid, which is easily effected by heating it with metallic copper—

$$\underset{\text{Hydrated sulphuric acid.}}{2(HO.SO_3)} + Cu = \underset{\text{Sulphate of copper.}}{CuO.SO_3} + 2HO + SO_2.$$

300 grains of copper clippings are heated in a Florence flask with 4 oz. (measured) of strong sulphuric acid, the gas being conducted by a bent tube down to the bottom of a dry bottle closed with a perforated card (see fig. 160, p. 147). Some time will elapse before the gas is evolved, for sulphuric acid acts upon copper only at a high temperature; but when the evolution of gas fairly commences, it will proceed very rapidly, so that it is necessary to remove the flame from under the flask. The gas will contain a little suspended vapour of sulphuric acid, which renders it turbid.

When the operation is finished, and the flask has been allowed to cool, it will be found to contain a grey crystalline powder at the bottom of a brown liquid. The latter is the excess of sulphuric acid employed, and retains very little copper, since sulphate of copper is insoluble in strong sulphuric acid. If the liquid be poured off, and the flask filled up with water, and set aside for some time, the crystalline powder will dissolve, forming a blue solution of sulphate of copper, yielding that salt in fine prismatic crystals by evaporation and cooling. The dark powder remaining undissolved after extracting the whole of the sulphate of copper consists chiefly of sulphide of copper, the production of which is interesting, as showing how far the deoxidising effect of the copper may be carried in this experiment.

Sulphurous acid is a very heavy (sp. gr. 2·25) colourless gas, characterised by its odour of burning brimstone. It condenses to a clear liquid at 0° F. (the temperature of a mixture of ice and salt) even at the ordinary pressure of the air, and has been frozen to a colourless crystalline solid at −105° F.

The liquefaction of the gas is easily exhibited by passing it down to the bottom of

a tube (A, fig. 187) closed at one end, and surrounded with a mixture of pounded ice with half its weight of salt. The tube should have been previously drawn out to a narrow neck at B, which may afterwards be sealed by the blowpipe, the lower part of the tube being still surrounded by the freezing mixture, since the liquid sulphurous acid boils at 14° F. The tube need not be very strong, for at the ordinary temperature the vapour of sulphurous acid exerts a pressure of only 2·5 atmospheres. Liquid sulphurous acid is a convenient agent for producing (by its rapid evaporation) the low temperature (− 39° F.) required to effect the solidification of mercury. A small globule of this metal may readily be frozen by dropping some liquid sulphurous acid upon it in a watch-glass placed in a strong draught of air. The tube containing the sulphurous acid should be held in a woollen cloth or glove. The attractive experiment of freezing water in a red-hot crucible may also be made with the liquid acid. A platinum crucible being heated to redness, and some liquid sulphurous acid poured into it, the liquid becomes surrounded with an atmosphere of sulphurous acid gas, which prevents its contact with the metal (assumes the *spheroidal* state), and its temperature is reduced by its own evaporation to so low a degree that a few drops of water allowed to flow into it will at once become converted into ice.

Fig. 187.

Sulphurous acid gas is very easily absorbed by water, as may be shown by pouring a little water into a bottle of the gas, closing the bottle with the palm of the hand, and shaking it violently (see fig. 148, p. 139), when the diminished pressure due to the absorption of the gas will cause the bottle to be sustained against the hand by the pressure of the atmosphere. Water absorbs 43·5 times its bulk of the gas at the ordinary temperature. If the solution be exposed to a low temperature, a crystallised hydrate of sulphurous acid is obtained, the composition of which does not appear to be accurately settled. When the solution of sulphurous acid is kept for some time in a bottle containing air, its smell gradually disappears, the acid absorbing oxygen and becoming converted into sulphuric acid.

Sulphurous acid, like carbonic acid, possesses in a high degree the power of extinguishing flame. A taper is at once extinguished in a bottle of the gas, even when containing a considerable proportion of air. One of the best methods of extinguishing burning soot in a chimney consists in passing up sulphurous acid by burning a few ounces of sulphur in a pan placed over the fire.

The principal uses of sulphurous acid depend upon its property of bleaching many animal and vegetable colouring matters. Although a far less powerful bleaching agent than chlorine, it is preferred for bleaching silk, straw, wool, sponge, isinglass, baskets, &c., which would be injured by the great chemical energy of chlorine. The articles to be bleached are moistened with water and suspended in a chamber in which sulphurous acid is produced by the combustion of sulphur. The colouring matters do not appear in general to be decomposed by the acid, but rather to form colourless combinations with it, for, in course of time, the original colour often reappears, as is seen in straw, flannel, &c., which become yellow from age, the sulphurous acid probably being oxidised into sulphuric acid. Stains of fruit and port wine on linen are conveniently removed by solution of sulphurous acid.

The red solution obtained by boiling a few chips of logwood with river water (*distilled water does not give so fine a colour*), serves to illustrate the bleaching proper-

ties of sulphurous acid. A few drops of the solution of the acid will at once change the red colour of the solution to a light yellow, but that the colouring power is suspended and not destroyed, may be shown by dividing the yellow liquid into two parts, and adding to them, respectively, potash and diluted sulphuric acid, which will restore the colour in a modified form. To contrast this with the complete decomposition of the colouring matter, a little sulphurous acid may be added to a weak solution of the permanganate of potash, when the splendid red solution at once becomes perfectly colourless, and neither acid nor alkali can effect its restoration, for in this case the red permanganic acid (Mn_2O_7), supposed to exist in the permanganate of potash, is reduced to the state of protoxide of manganese.

Fig. 188.

If a bunch of damp coloured flowers be suspended in a bell-jar over a crucible containing a little burning sulphur (fig. 188), many of the flowers will be completely bleached by the sulphurous acid, and by plunging them afterwards into diluted sulphuric acid and ammonia, their colours may be partly restored, with some very curious modifications.

Another very useful property of sulphurous acid is that of arresting fermentation (or putrefaction), apparently by killing the vegetable or animal growth which is the cause of the fermentation. This is commonly designated the *antiseptic* property of sulphurous acid, and is turned to account when casks for wine or beer are *sulphured* in order to prevent the action of any substance contained in the pores of the wood, and capable of exciting fermentation, upon the fresh liquor to be introduced. If a little solution of sugar be fermented with yeast in a flask provided with a funnel tube (fig. 189), a solution of sulphurous acid poured in through the latter will at once arrest the fermentation. The salts of sulphurous acid (sulphites) are also occasionally used to arrest fermentation, in the manufacture of sugar, for instance. Clothes are sometimes fumigated with sulphurous acid to destroy vermin.

Fig. 189.

The disposition of sulphurous acid to absorb oxygen and pass into sulphuric acid, renders it a powerful deoxidising or reducing agent. Solutions of silver and gold are reduced to the metallic state by sulphurous acid if a very little ammonia be added, and a gentle heat applied.

If a solution of sulphurous acid be heated for some time in a sealed tube to 340° F. one portion of the acid deoxidises another, sulphur is separated, and sulphuric acid formed; $3SO_2 + 2HO = 2(HO.SO_3) + S$.

Sulphurous acid gas combines with ammonia gas to form two solid compounds ($NH_3.SO_2$, and $NH_3.2SO_2$) which are quite different in their properties from the sulphite and bisulphite of ammonia ($NH_3.HO.SO_2$, and $NH_3.HO.2SO_2$), which are formed when sulphurous acid acts upon solution of ammonia.

Chlorine combines with an equal volume of sulphurous acid, under the influence of bright sunshine, to produce a colourless liquid, the vapour of which is very acrid and irritating to the eyes. Its composition is represented by SO_2Cl, and it is sometimes called *chlorosulphuric acid*, though it does not combine with bases, and is decomposed by water, yielding hydrochloric and sulphuric acids. It is also known as *chloride of sulphuryle*, SO_2 being looked upon as the radical of sulphuric acid. The *chloride of thionyle*, $SOCl$, is a colourless volatile liquid obtained by the action of

hypochlorous acid gas on sulphur dissolved in the subchloride of sulphur. It is decomposed by water, yielding hydrochloric and sulphurous acids.

Potassium and sodium, when heated in sulphurous acid, burn vividly, producing the oxides and sulphides of the metals.

Iron, lead, tin, and zinc are also converted into oxides and sulphides when heated in sulphurous acid; $SO_2 + Zn_3 = ZnS + 2ZnO$.

Sulphites.—The acid character of sulphurous acid is rather feeble, although stronger than that of carbonic acid. There is much general resemblance between the sulphites and carbonates, in point of solubility, the sulphites of the alkali-metals being the only salts of sulphurous acid which are freely soluble in water. Sulphurous acid, like carbonic, forms two classes of salts, the sulphites (for example, sulphite of soda, $NaO . SO_2$) and bisulphites (as bisulphite of potash, $KO . HO . 2SO_2$).

The *sulphite of soda* is extensively manufactured for the use of the paper-maker, who employs it as an *antichlore* for *killing the bleach*, that is, neutralising the excess of chlorine after bleaching the rags with chloride of lime and sulphuric acid (see p. 145)—

$$NaO . SO_2 + HO + Cl = NaO . SO_3 + HCl .$$

It is prepared by passing sulphurous acid over damp crystals of carbonate of soda, when the carbonic acid is expelled, and sulphite of soda formed, which is dissolved in water and crystallised. It forms oblique prisms having the composition $NaO . SO_2 + 7Aq$, which effloresce in the air, becoming opaque, and slowly absorbing oxygen, passing into sulphate of soda ($NaO . SO_3$). Its solution is slightly alkaline to test-papers.

For the manufacture of sulphite of soda, the sulphurous acid is obtained either by the combustion of sulphur or by heating sulphuric acid with charcoal—

$$2(HO . SO_3) + C = 2HO + CO_2 + 2SO_2 .$$

The carbonic acid, of course, will not interfere with this application of the sulphurous acid.

145. *Composition of sulphurous acid.*—When sulphur is burnt in oxygen, the volume of the sulphurous acid produced is equal to that of the oxygen, so that 1 vol. of sulphurous acid contains 1 vol. of oxygen.

The weight of 1 vol. (sp. gr.) of sulphurous acid is, .	2·2470
Deducting the weight of 1 vol. (sp. gr.) of oxygen, .	1·1056
	1·1414

The remainder represents the weight of sulphur vapour contained in one volume of sulphurous acid. But it has been seen (p. 195) that the weight of one volume of sulphur vapour (at 1900° F.) is 2·23, so that the above weight represents half a volume of sulphur vapour; and 2 vols. of sulphurous acid contain 2 vols. of oxygen and 1 vol. of sulphur vapour.

The quantity of sulphurous acid which generally combines with one equivalent of a base amounts to 32 parts by weight, which may, therefore, be taken as the equivalent weight of sulphurous acid. This weight would occupy twice the volume of 8 parts by weight of oxygen.

One equivalent of sulphurous acid, therefore, representing 32 parts by weight or 2 vols., contains 1 eq. (16 parts by weight) or 1 vol. of sulphur vapour, and 2 eqs. (16 parts by weight) or 2 vols. of oxygen.

The *molecular formula of sulphurous acid* would be $S\Theta_2$ ($S = 32, \Theta = 16$)

representing 2 vols. of the gas (H = 1 vol.), containing 1 vol. (or 1 atom) of sulphur vapour and 2 vols. (or 2 atoms) of oxygen.

Just as in the case of carbonic acid (see p. 75), many chemists deny the acid nature of the compound SO_2 altogether, and term it *sulphurous anhydride*, reserving the name of sulphurous acid for the hydrated sulphurous acid, $HO.SO_2$ or HSO_3 (or $H_2S\Theta_3$), obtained by exposing the aqueous solution of sulphurous acid to a very low temperature.

Sulphuric Acid.

146. It has been already noticed that one of the most abundant forms in which sulphur occurs in nature is that of sulphuric acid in combination with certain bases. Hydrated sulphuric acid has also been found in certain springs and rivers in volcanic regions. Sulphurous acid and oxygen gases combine to form sulphuric acid (SO_3) when passed through a tube containing heated platinum or certain metallic oxides, such as those of copper and chromium, the action of which in promoting the combination is not thoroughly understood.

The combination may be shown by passing oxygen from the tube A (fig. 190) connected with a gas-holder, through a strong solution of sulphurous acid (B), so that it may take up a quantity of that gas, afterwards through a tube (C) containing pumice stone soaked with oil of vitriol, to remove the water, and then through a bulb (D) containing platinised asbestos (see p. 132). The mixture of the gases issuing into the air is quite invisible, but when the bulb is gently heated, combination takes place, and dense white clouds are formed in the air, from the combination of the anhydrous sulphuric acid (SO_3) produced, with the atmospheric moisture.

Fig. 190.

An easier method of obtaining the anhydrous sulphuric acid will be noticed hereafter, but the hydrated acid is of so much more importance that its preparation and properties should be studied before those of the anhydrous acid.

Hydrated sulphuric acid.—More than four centuries ago, the alchemist Basil Valentine subjected *green vitriol*, as it was then called (sulphate of iron), to distillation, and obtained an acid liquid which he named *oil of vitriol*. The process discovered by this laborious monk is even now in use at Nordhausen in Saxony, and the *Nordhausen oil of vitriol* is an important article of commerce. The crystals of sulphate of iron ($FeO.SO_3 + 7HO$) are exposed to the air so that they may absorb oxygen, and become converted into the *basic persulphate of iron*—

$$2(FeO.SO_3) + O = \underset{\text{Basic persulphate of iron.}}{Fe_2O_3.2SO_3}.$$

This salt is dried, and distilled in earthen retorts, the oil of vitriol being condensed in receivers of glass or stoneware. The action of heat upon the basic persulphate of iron separates the acid from the base, and the salt were absolutely dry, the anhydrous sulphuric acid would be *pected to* distil over. There is always enough water, however, left in

the persulphate, to combine with the anhydrous acid to form the Nordhausen oil of vitriol, the composition of which is pretty correctly expressed by the formula $HO.2SO_3$. The peroxide of iron (Fe_2O_3) which is left in the retorts, is the red powder known as *colcothar*, which is used for polishing plate glass and metals.

The green vitriol employed for preparing the Nordhausen acid is obtained from iron pyrites (FeS_2). A particular variety of this mineral, *white pyrites* (or efflorescent pyrites), when exposed to moist air, undergoes oxidation, yielding sulphate of iron and sulphuric acid—

$$FeS_2 + HO + O_7 = FeO.SO_3 + HO.SO_3.$$

Large masses of this variety of pyrites in mineralogical cabinets may often be seen broken up into small fragments, and covered with an acid efflorescence of sulphate of iron from this cause. Ordinary iron pyrites is not oxidised by exposure to the air unless it be first subjected to distillation in order to separate a portion of the sulphur which it contains.

The Nordhausen acid is readily distinguished from English sulphuric acid by its fuming in the air, when the bottle is opened. This is due to the escape of a little vapour of anhydrous sulphuric acid. It is heavier than the English acid, its specific gravity being 1·9. It is chiefly used for dissolving indigo in preparing the Saxony blue dye, and is a convenient source of the anhydrous sulphuric acid; for if it be gently heated in a retort, the anhydrous acid is disengaged, and may be condensed in silky crystals in a receiver kept cool by ice, whilst ordinary hydrated sulphuric acid ($HO.SO_3$) is left in the retort.

The process adopted at Nordhausen, though simple in theory, is expensive on account of the consumption of fuel and the breaking of the retorts, so that the price of the acid, compared with that of English manufacture, is very high.

The first step towards the discovery of our present process was also made by Valentine, when he prepared his *oleum sulphuris per campanum*, by burning sulphur under a bell-glass over water, and evaporating the acid liquid thus obtained. The same experimenter also made a very important advance when he burnt a mixture of sulphur, sulphide of antimony, and nitre, under a bell-glass placed over water; but it was not until the middle of the eighteenth century that it was suggested by some French chemists to burn the sulphur and nitre alone over water, a process by which the acid appears actually to have been manufactured upon a pretty large scale. The substitution of large chambers of lead for glass vessels by Dr Roebuck was a great improvement in the process, and about the year 1770 the preparation of the acid formed an important branch of manufacture; since then the process has been steadily improving, until, at the present time, upwards of 100,000 tons are annually consumed in Great Britain, and a very large quantity is exported. The diminution in the price of oil of vitriol well exhibits the progress of improvement in its production, for the original *oil of sulphur* appears to have been sold for about half-a-crown an ounce, and that prepared by burning sulphur with nitre in glass vessels at the same price per pound; but when leaden chambers were introduced, the price fell to a shilling per pound, and at present oil of vitriol can be purchased at the rate of five farthings per pound.

The description of the present process of manufacture will be best understood after a consideration of the chemical changes upon which it depends.

It has been seen that when sulphur is burnt in air, sulphurous acid is

the chief product. When sulphurous acid acts upon hydrated nitric in the presence of water, sulphuric acid and nitric oxide are formed-

$$3SO_2 + HO.NO_5 + 2HO = 3(HO.SO_3) + NO_2.$$

Nitric oxide, in contact with air, combines with its oxygen to nitric peroxide (NO_4).

If nitric peroxide is brought into contact with sulphurous aci water, it is again converted into nitric oxide with formation of sul acid—

$$NO_4 + 2SO_2 + 2HO = NO_2 + 2(HO.SO_3).$$

It appears, therefore, that nitric oxide may be employed to oxygen from the air, and to convey it to the sulphurous acid, so theoretically, an unlimited quantity of sulphurous acid, supplied wi and water, might be converted into sulphuric acid by a given quan nitric oxide.

To illustrate these important chemical principles of the manufacture of sul acid, the following experiments may be performed :—

I. A quart bottle of nitric oxide (p. 130) is placed mouth to mouth with bottle of oxygen, when both bottles will be filled with the red nitric peroxide

II. The quart bottle of this red gas is placed mouth to mouth with a quar of sulphurous acid gas (fig. 191), when the red colour will soon disappear, sides of the bottles will be covered with a cry substance formed by the reaction between th peroxide, the sulphurous acid, and the small q of water present in the gases. The true c tion of this crystalline body is doubtful, for the purpose of the present reasoning, it garded as $NO_2.2SO_3.HO$, its formation w represented by the equation—

Fig. 191.

$$NO_4 + 2SO_2 + HO = NO_2.2SO$$

III. A little water is shaken round the in the bottles, when the crystalline compound decomposed with effervescence, evolving nitri and producing hydrated sulphuric acid—

$$NO_2.2SO_3.HO + HO = NO_2 + 2(HO.$$

IV. Air is blown into the bottles through a glass tube, when the presence nitric oxide will be proved by the formation of the red nitric peroxide.

Fig. 192.—Preparation of sulphuric acid.

In the presence of abu of water this crystallin pound is not produced, be shown by the followin fication of the experime

V. A large glass fl globe (A, fig. 192) is fitt a cork, through whic passed—

(*a*) a tube connected flask (D) containing cop strong sulphuric acid, fo ing sulphurous acid ;

(*b*) a tube connected flask (B) containing cop diluted nitric acid (sp. for supplying nitric oxi

(*c*) a tube proceedin a small flask (E) con water.

On applying a gentle heat to the flask containing nitric acid and copper, th

xide passes into the globe and combines with the oxygen of the air, filling the globe with red nitric peroxide. The nitric oxide flask may then be removed. Sulphurous acid is then generated by heating the flask containing sulphuric acid and copper; the sulphurous acid will soon decolorise the red nitric peroxide, the contents of the globe becoming colourless, and the crystalline compound forming abundantly on the sides: the sulphurous acid flask may then be removed. Steam is sent into the globe from the flask containing water, when the crystalline compound will be dissolved, and sulphuric acid will collect at the bottom of the globe. If air be now blown into the globe, the nitric oxide will again acquire the red colour of nitric peroxide.

If the experiment be repeated, the steam being introduced simultaneously with the sulphurous acid, no crystalline compound whatever will be formed, the sulphurous acid being at once converted into hydrated sulphuric acid.

Since the cork is somewhat corroded in this experiment, it is preferable to have the mouth of the flask ground and closed by a ground glass plate, perforated with holes for the passage of the tubes. The perforations are easily made by placing the glass plate flat against the wall and piercing it with the point of a revolving rat's-tail file dipped in turpentine; the file is then gradually worked through the hole until the latter is of the required size.

The process employed for the manufacture of English oil of vitriol will now be easily understood.

A series of chambers is constructed of leaden plates, the edges of which are united by autogenous soldering (that is, by fusing their edges, without solder, which would be rapidly corroded by the acid vapours); the leaden chambers are supported and strengthened by a framework of timber (fig. 193).

The *sulphurous acid* is generated by burning sulphur or iron pyrites in a suitable furnace (A) adjoining the chambers, and so arranged that the sulphurous acid produced may be mixed with about the proper quantity *of air* to furnish the oxygen required for its conversion into sulphuric acid.

Nitric acid vapour is evolved from a mixture of nitrate of soda and oil of vitriol (see p. 124) contained in an iron pan which is heated by the combustion of the sulphur, so that the nitric acid is carried into the chambers with the current of sulphurous acid and air.

Water covers the floor of the chambers to the depth of about two inches, and jets of steam are introduced at different parts from an adjacent boiler (B).

The sulphurous acid acts upon the nitric acid vapour, in the presence of the water, forming nitric oxide and hydrated sulphuric acid, which rains down into the water on the floor of the chambers—

$$3SO_2 + HO.NO_5 + 2HO = NO_2 + 3(HO.SO_3) .$$

If this nitric oxide were permitted to escape from the chambers, and a fresh quantity of nitric acid vapour introduced to oxidise another portion of sulphurous acid, it is evident that 1 eq. (85 parts by weight) of nitrate of soda would be required to furnish the nitric acid for the conversion of 3 eqs. (48 parts by weight) of sulphur, whereas, in practice, 3 parts by weight only of nitrate of soda are employed for 48 parts of sulphur.

For the nitric oxide (NO_2) at once acquires oxygen from the air admitted together with the sulphurous acid, and becomes nitric peroxide (NO_4), which oxidises more sulphurous acid in the presence of water, converting it into hydrated sulphuric acid—

$$2SO_2 + NO_4 + 2HO = 2(HO.SO_3) + NO_2 .$$

A great reduction in the volume of the gas in the chamber thus takes place (*4 vols. SO_2 and 4 vols. NO_4 yielding* 4 vols. NO_2), so that there

is room for the introduction of a fresh quantity of the mixture of sulphurous acid and air from the furnace, upon which the nitric oxide acts as before, taking up the oxygen from the air and handing it over to the sulphurous acid, in the presence of water, to produce a fresh supply of hydrated sulphuric acid.

But the nitrogen of the air takes no part in these changes, and since

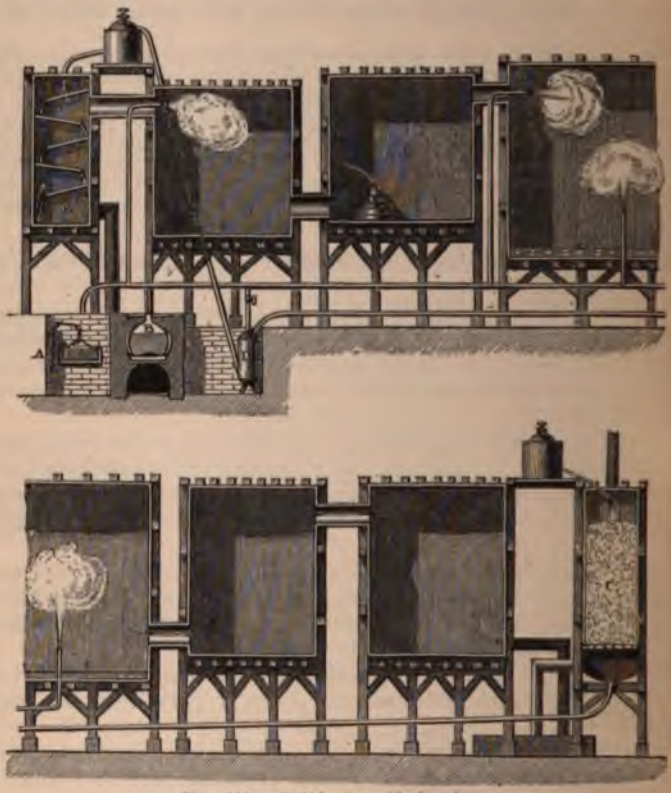


Fig. 193.—Sulphuric acid chambers.

the oxygen consumed in converting the sulphur into sulphuric acid is accompanied by four times its volume of nitrogen, a very large accumulation of this gas takes place in the chambers, and provision must be made for its removal in order to allow space for those gases which take part in the change. The obvious plan would appear to be the erection of a simple chimney for the escape of the nitrogen at the opposite end of the chamber to that at which the sulphurous acid and air enter it; and this plan was formerly adopted, but the nitrogen carries off with it a portion of the nitric oxide which is so valuable in the chamber, and to save this the escaping nitrogen is now generally passed through a leaden chamber (C) filled with coke, over which oil of vitriol is allowed to trickle; the oil of vitriol absorbs the nitric oxide, and flows into a cistern (D), from which it is pumped up to the top of another chamber (E) filled with coke, *arranged* with shelves in cascade, through which the hot sulphurous

ir are made to pass as they enter, when they take up the nitric oxide
he oil of vitriol, and carry it with them into the chamber.
ore the introduction of this plan of retaining the nitric oxide by oil
riol, it required a quantity of nitrate of soda amounting to $\frac{1}{8}$th or
of the weight of the sulphur to convert it into sulphuric acid, whereas
$\frac{1}{16}$th or even less is now often made to suffice.
sulphuric acid is allowed to collect on the floor of the chamber
it has a specific gravity of about 1·6, and contains 70 per cent. of oil
riol ($HO . SO_3$). If it were allowed to become more concentrated
this, it would absorb some of the nitric oxide in the chamber, so
t is now drawn off.
is acid is quite strong enough for some of the applications of sul-
c acid, particularly for that which consumes the largest quantity in
ountry, viz., the conversion of common salt into sulphate of soda as
iminary step in the manufacture of carbonate of soda. To save the
se of transporting the acid for this purpose, the *vitriol chambers*
part of the plant of the alkali works.
convert this weak acid into the ordinary oil of vitriol of commerce,
un off into shallow leaden pans set in brickwork, and supported on
ars over the flue of a furnace, where it is heated until so much
has evaporated that the specific gravity of the acid has increased to
The concentration cannot be carried further in leaden pans, be-
the strong acid acts upon the lead, and converts it into sulphate—

$$2(HO . SO_3) + Pb = PbO . SO_3 + 2HO + SO_2 .$$

acid of 1·72 sp. gr. contains about 80 per cent. of true oil of vitriol
SO_3), and is largely employed for making superphosphate of lime,
other rough chemical manufactures. It is technically called *brown*
having acquired a brown colour from organic matter accidentally
t in it.
convert this brown acid into commercial oil of vitriol, it is boiled
either in glass retorts or platinum stills, when water distils over,
panied by a little sulphuric acid, and the acid in the retort becomes
less, the brown carbonaceous matter being oxidised by the strong
uric acid, with formation of carbonic and sulphurous acids. When
white fumes of oil of vitriol begin to pass over, showing that all the
luous water has been expelled, the acid is drawn off by a siphon.
very diluted acid which distils off is employed instead of water on
or of the leaden chamber.

cost of the acid is very much increased by this concentration. It cannot be
ted in open vessels, partly on account of the loss of sulphuric acid, partly be-
concentrated sulphuric acid absorbs moisture from the open air even at the
point. The loss by breakage of the glass retorts is very considerable, al-
it is reduced as far as possible by heating them in sand, and keeping them
at about the same temperature by supplying them with hot acid. But the
point of the concentrated acid is very high (640° F.), and the retorts conse-
y become so hot that a current of cold air or an accidental splash of acid will
ntly crack them at once. Moreover, the acid boils with *succussion* or violent
ng, caused by sudden bursts of vapour, which endanger the safety of the retort.
h platinum stills the risk of fracture is avoided, and the distillation may be
ted more rapidly, the brown acid (sp. gr. 1·72) being admitted at the top,
e oil of vitriol (sp. gr. 1·84) drawn off by a platinum siphon from the bottom
still, which is protected from the open fire by an iron jacket. But since a
m still will cost £2000 or £3000, the interest upon its value increases the
production of the acid.

When the perfectly pure acid is required, it is actually distilled over a
leave the solid impurities (sulphate of lead, &c.,) behind in the retort.
fragments of rock crystal should be introduced into the retort to modera
bursts of vapour, and heat applied by a ring gas-burner with somewhat di
jets.

Divested of working details, this most important chemical manuf
may be thus described :—

A mixture of sulphurous acid, air, steam, and a little vapour of
acid, is introduced into a leaden chamber containing a layer of water.
nitric acid is reduced by the sulphurous acid to the state of nitric
(NO_2), which takes up oxygen from the air (forming NO_4), and give
the sulphurous acid, which it converts into sulphuric acid. This
sorbed by the water, forming diluted sulphuric acid, which is concent
by evaporation, first in leaden pans, and afterwards in glass reto
platinum stills.

Properties of oil of vitriol.—The properties of concentrated sulp
acid are very characteristic. Its great weight (sp. gr. 1·842), freedom
odour, and oily appearance, distinguish it from any other liquid comm
met with, which is fortunate, because it is difficult to preserve a label
the bottles of this powerfully corrosive acid. Although, if absolutely
it is perfectly colourless, the ordinary acid used in the laboratory
peculiar grey colour, due to traces of organic matter. Its high bo
point (640° F.) has been already noticed; and although its vapour i
fectly transparent in the vessel in which the acid is boiled, as soon
issues into the air it condenses into voluminous dense clouds of a
irritating description. Even a drop of the acid evaporated in an ope
will fill a large space with these clouds. Oil of vitriol solidifies
cooled to about −30° F., but the acid once solidified requires a
higher temperature to liquefy it again. Oil of vitriol rapidly corrod
skin and other organic textures upon which it falls, usually chan
blackening them at the same time. Poured upon a piece of woo
latter speedily assumes a dark brown colour; and if a few lumps of
be dissolved in a very little water, and stirred with oil of vitriol, a
action takes place, and a semi-solid black mass is produced. Th
perty of sulphuric acid is turned to account in the manufacture of
ing, in which treacle and oil of vitriol are employed. These effects
be ascribed to the powerful attraction of oil of vitriol for water.
fibre ($C_{12}H_{10}O_{10}$) (which composes the bulk of wood, paper, and
and sugar ($C_{12}H_{11}O_{11}$), may be regarded, for the purpose of this e
tion, as composed of carbon associated with 10 and 11 equival
water, and any cause tending to remove the water would tend to eli
the carbon.

The great attraction of this acid for water is shown by the high
rature (often exceeding the boiling point of water) produced on
oil of vitriol with water, which renders it necessary to be careful in
ing the acid.

The water should be placed in a jug, and the oil of vitriol poured int
thin stream, a glass rod being used to mix the acid with the water as it
Ordinary oil of vitriol becomes turbid when mixed with water, from the
tion of sulphate of lead (formed from the evaporating pans), which is so
the concentrated but not in the diluted acid, so that if the latter be all
stand for a few hours, the sulphate of lead settles to the bottom, and the cl
may be poured off free from lead. Diluted sulphuric acid has a smaller bu
is occupied by the acid and water before mixing.

Even when largely diluted, sulphuric acid corrodes textile fabrics very idly, and though the acid be too dilute to appear to injure them at st, it will be found that the water evaporates by degrees, leaving the id in a more concentrated state, and the fibre is then perfectly rotten. he same result ensues at once on the application of heat; thus, if charac- rs be written on paper with the diluted acid, they will remain invisible ntil the paper is held to the fire, when the acid will char the paper, and e writing will appear intensely black.

If oil of vitriol be left exposed to the air in an open vessel, it very soon creases largely in bulk from the absorption of water, and a flat dish of l of vitriol under a glass shade (fig. 194) is frequently employed in the boratory for drying substances with- t the assistance of heat. The drying of course much accelerated by plac- the dish on the plate of an air- mp, and exhausting the air from shade, so as to effect the drying *vacuo*. It will be remembered o that oil of vitriol is in constant for drying gases.

Fig. 194.—Drying over oil of vitriol.

At a red heat, the vapour of oil vitriol is decomposed into water, phurous acid, and oxygen—

$$HO.SO_3 = HO + SO_2 + O.$$

is decomposition takes place most easily when the vapour is passed rough a strongly-heated tube of platinum, and it has been taken advan- e of for the preparation of oxygen, the sulphurous acid being absorbed passing the mixed gases through lime. Reflecting upon the manufac- e of oil of vitriol, it will be perceived that the oxygen thus obtained s originally derived from the air.

When sulphur is boiled with oil of vitriol, the latter gradually dissolves melted sulphur, converting it into sulphurous acid—

$$S + 2(HO.SO_3) = 3SO_2 + 2HO.$$

All ordinary metals are acted upon by concentrated sulphuric acid when ated, except gold and platinum (this last even does not quite escape en long boiled with the acid), the metal being oxidised by one portion the acid, which is thus converted into sulphurous acid, the oxide com- ing with another part of the sulphuric acid to form a sulphate. Thus, en silver is boiled with strong sulphuric acid, it is converted into sul- ate of silver, which is soluble in hot water—

$$Ag + 2(HO.SO_3) = AgO.SO_3 + 2HO + SO_2.$$

ould the silver contain any gold, it is left behind in the form of a dark wder. Sulphuric acid is extensively employed for the separation or *rting* of silver and gold. This acid is also employed for extracting gold m copper; and when sulphate of copper is manufactured by dissolving t metal in sulphuric acid (see p. 196), large quantities of gold are netimes extracted from the accumulated residue left undissolved by the d.

If the sulphuric acid contains nitric acid, it dissolves a considerable antity of gold, which separates again in the form of a purple powder *en the acid is diluted with water.*

Some of the uses of sulphuric acid depend upon its specific actic certain organic substances, the nature of which has not yet been cl explained. Of this kind is the conversion of paper into *vegetable p ment* by immersion in a cool mixture of two measures of oil of vitrio one measure of water, and subsequent washing. The conversion i attended by any change in the weight of the paper.

Beside oil of vitriol, sulphuric acid forms other definite combina with water. By evaporating diluted sulphuric acid *in vacuo* at 212 an acid is left which has the composition $HO . SO_3 + 2HO$ (sp. gr. 1· If this acid be evaporated in air at 400° F., as long as steam escapes, remaining acid has the composition $HO . SO_3 + HO$ (sp. gr. 1·78). acid is called *glacial sulphuric acid*, because it solidifies to a mass of like crystals at 47° F.

*Composition of oil of vitriol.**—It is found by experiment that in o to neutralise 1 equivalent (47 parts by weight) of potash (KO) t are required 49 parts by weight of oil of vitriol. If 49 parts of o vitriol be heated with a weighed quantity of pure oxide of lead, n than sufficient to combine with the acid, 9 parts of water are expe and the weight of the oxide of lead is increased by 40. One equiva (49 parts by weight) of oil of vitriol, therefore, contains 40 part equivalent = 16 sulphur + 24 oxygen) of anhydrous sulphuric acid, 9 parts (1 equivalent) of water. The specific gravity (or weight volume) of vapour of oil of vitriol (at 880°) is stated to be 1·692, so 1 equivalent (49 parts) would occupy 4 volumes (8 parts O = 1 volum

Weight of 4 volumes $HO . SO_3$	(1·692 × 4)	= 6·768
Weight of 2 volumes HO	(·622 × 2)	= 1·244
		5·524

The difference (5·524) represents the weight of the vapour of anhy sulphuric acid contained in 4 volumes of vapour of oil of vitriol.

Experiment has proved that when the vapour of anhydrous sulp acid is passed through red-hot porcelain tubes, it yields a mixtur volumes of sulphurous acid and 1 volume of oxygen, showing it t tain 1 equivalent of SO_2 (= 1 equivalent or 1 volume of sulphu 2 equivalents or 2 volumes of oxygen) and 1 equivalent of ox hence the anhydrous sulphuric acid contains

1 volume sulphur vapour, weighing		2·2300
3 volumes oxygen	,,	3·3168
		5·5468

Now the weight of 1 volume (sp. gr.) of vapour of anhydrous sulp acid has been found by experiment to be 3·01, so that it would a that the above number (5·54) really represents 2 volumes of the v though the difference is somewhat greater than usual, between the r of experiment and calculation.

The number 5·546, however, closely approximates to that above (5·524), as representing the weight of the vapour of the anhydrou contained in 4 volumes of vapour of oil of vitriol.

* Pure oil of vitriol ($HO . SO_3$) can only be obtained by crystallisation, for when trated by boiling, a portion of the hydrate is decomposed, anhydrous sulphuric acid *off, until* the residual acid in the retort contains 98·7 per cent. of $HO . SO_3$.

would appear, therefore, that 4 volumes (1 equivalent) of vapour
il of vitriol contain 2 volumes (1 equivalent) of vapour of water,
2 volumes (1 equivalent) of vapour of anhydrous sulphuric acid, or
lumes of hydrogen (contained in 2 volumes HO), 1 volume of sulphur,
4 volumes of oxygen (3 volumes belonging to the SO_3, and 1 volume
e HO).

he *molecular formula* of oil of vitriol would therefore be written
. $S\Theta_3$ or $H_2S\Theta_4$ ($S = 32$, $\Theta = 16$). This formula would represent
lecule of the acid to occupy 4 volumes ($H = 1$ volume) instead of
e ordinary molecular volume of compound vapours. Some chemists
ain this by assuming that the oil of vitriol vapour is decomposed into
r and anhydrous sulphuric acid at the temperature (880° F.) at which
ecific gravity is determined.

7. *Anhydrous sulphuric acid* or *sulphuric anhydride.*—The mode of
aring this substance from the fuming sulphuric acid has already been
ed. It is more commonly obtained by expelling the water from bi-
ate of soda ($NaO . HO . 2SO_3$) by fusing it at a dull red heat, and
wards distilling the anhydrous bisulphate ($NaO . 2SO_3$) in an earthen
t, when neutral sulphate of soda ($NaO . SO_3$) is left, and the anhydrous
uric acid passing off as vapour may be condensed in a receiver cooled
e.

hydrous sulphuric acid forms a white mass of crystals resembling
tos; it fumes when exposed to air, since it emits vapour which con-
s the moisture of the air, and it soon deliquesces from absorption of
, becoming hydrated sulphuric acid. When thrown into water it
s like red-hot iron from the sudden formation of steam. It fuses at
., and boils at 110° F. The vapour is decomposed, as mentioned
, into sulphurous acid and oxygen when passed through a red-hot
Phosphorus burns in its vapour, combining with the oxygen and
ting sulphur. Baryta glows when heated in the vapour of anhydrous
uric acid, and combines with it to form sulphate of baryta.

hydrous sulphuric acid is capable of combining with olefiant gas
) and oil-gas (C_3H_4), and absorbs these from mixtures of gases.
e analysis of coal-gas, a fragment of coke wetted with Nordhausen
uric acid is passed up into a measured volume of the gas standing
mercury, to absorb these illuminating hydrocarbons.

interesting method of obtaining the anhydrous sulphuric acid con-
n pouring 2 parts by weight of oil of vitriol over 3 parts of anhydrous
horic acid, contained in a retort cooled in ice and salt, and after-
s distilling at a gentle heat, when the phosphoric acid retains the
, and the anhydrous sulphuric acid may be condensed in a cooled
er.

8. *Sulphates. Action of sulphuric acid upon metallic oxides.*—At
ion temperatures sulphuric acid has a more powerful attraction for
than any other acid, and is therefore capable of displacing all other
from their salts; many cases will be remembered in which this power
phuric acid is turned to account.

great is the acid energy of sulphuric acid, that when it is allowed
upon an indifferent or acid metallic oxide, it causes the separa
art of the oxygen, and combines with the basic oxide so prod
ntage is sometimes taken of this circumstance for the prepara

oxygen; for instance, when binoxide of manganese is heated with phuric acid, sulphate of manganese is produced, and oxygen disengag

$$MnO_2 + HO.SO_3 = MnO.SO_3 + O + HO.$$

Again, if chromic acid be treated in the same way, sulphate of sesquio of chromium will be produced, with liberation of oxygen—

$$2CrO_3 + 3(HO.SO_3) = Cr_2O_3.3SO_3 + O_3 + 3HO.$$

A mixture of bichromate of potash ($KO.2CrO_3$) and sulphuric ac sometimes used as a source of oxygen.

Many bases are capable of forming two salts with sulphuric ac neutral sulphate and an acid sulphate. The acid sulphates may be re sented as compounds of the neutral sulphates with hydrated sulph acid; thus, the neutral sulphate of potash is $KO.SO_3$, and the bisulp is $KO.SO_3, HO.SO_3$. The latter, being a solid salt which possess high temperatures, almost all the acid energy of sulphuric acid, is u useful in blowpipe and metallurgic experiments. When strongly he this salt parts with hydrated sulphuric acid, and neutral sulphate of ash is left. It has been seen that bisulphate of soda ($NaO.SO_3, HO.$ parts with its water when heated, and becomes $NaO.2SO_3$. Cry of anhydrous bisulphate of potash $KO.2SO_3$ have also been obtained

Sulphuric acid forms a large number of double salts in which tw phates are combined together. The large class of *alums* yields exam of these, in which one of the sulphates contains an alkaline base, an other a basic sesquioxide. *Potash-alum*, for example, is represente the formula $KO.SO_3, Al_2O_3.3SO_3 + 24Aq$, being a double sul of alumina and potash.

In consequence of the tendency of sulphuric acid to break up int phurous acid and oxygen at a high temperature, most of the sulphat decomposed by heat; sulphate of copper, for example, when very str heated, leaves oxide of copper, whilst sulphurous acid and oxygen es $CuO.SO_3 = CuO + SO_2 + O$. Sulphate of iron is more decomposed, because of the attraction of the protoxide of iron fo oxygen, with which it combines to form sesquioxide—

$$2(FeO.SO_3) = Fe_2O_3 + SO_2 + SO_3$$

part of the acid escaping in the anhydrous state.

Sulphate of zinc ($ZnO.SO_3$) has been proposed as a source of o upon the large scale, since it is a very cheap salt, and when st heated, yields a residue of oxide of zinc which is useful as a white whilst sulphurous acid and oxygen gases escape, the former of whic be absorbed by lime or soda, yielding sulphites which are useful arts.

The neutral sulphates of potash, soda, baryta, strontia, lime, and of lead are not decomposed by heat, and sulphate of magnesia i partly decomposed at a very high temperature.

When a sulphate is heated with charcoal, the carbon removes the of the oxygen, and a sulphide of the metal remains, thus—

$$\underset{\text{Sulphate of potash.}}{KO.SO_3} + C_4 = \underset{\text{Sulphide of potassium.}}{KS} + 4CO.$$

rogen, at a high temperature, effects a similar decomposition.

he ordinary temperature, sulphate of lime in solution is some-
lised by organic matter; this may occasionally be noticed in
rer waters when kept in closed vessels; they acquire a strong
lrosulphuric acid, in consequence of the conversion of a part
ate of lime into sulphide of calcium by the organic constitu-
vater, and the subsequent decomposition of the sulphide of
he carbonic acid present in the water.
wing table exhibits the composition of the sulphates most
et with :—

me.	Common Name.	Equivalent Formula.	Atomic Unitary Formula.
otash	Sal polychrest	$KO . SO_3$	$K_2S\Theta_4$
da	Glauber's salt	$NaO . SO_3 + 10HO$	$Na_2S\Theta_4 . 10H_2\Theta$
potash		$KO . SO_3, HO . SO_3$	$KHS\Theta_4$
am-		$NH_3 . HO . SO_3$	$(NH_4)_2S\Theta_4$
aryta	Heavy spar	$BaO . SO_3$	$BaS\Theta_4$
me	Gypsum	$CaO . SO_3 + 2HO$	$CaS\Theta_4 . 2H_2\Theta$
nag-	Epsom salts	$MgO . SO_3 + 7HO$	$Mg . S\Theta_4 . 7H_2\Theta$
hate and	Potash-alum	$KO . SO_3, Al_2O_3 . 3SO_3 + 24HO$	$KAl\,2S\Theta_4 . 12H_2\Theta$
hate and	Ammonia-alum	$NH_3 . HO . SO_3, Al_2O_3 . 3SO_3 + 24HO$	$NH_4Al2S\Theta_4 . 12H_2\Theta$
hate ium	Chrome-alum	$KO . SO_3, Cr_2O_3 . 3SO_3 + 24HO$	$K\Theta r\,2S\Theta_4 . 12H_2\Theta$
on	Green vitriol, Copperas	$FeO . SO_3 + 7HO$	$FeS\Theta_4 . 7H_2\Theta$
an-		$MnO . SO_3 + 5HO$	$MnS\Theta_4 . 5H_2\Theta$
nc	White vitriol	$ZnO . SO_3 + 7HO$	$ZnS\Theta_4 . 7H_2\Theta$
ad		$PbO . SO_3$	$PbS\Theta_4$
pper	Blue vitriol, Blue stone	$CuO . SO_3 + 5HO$	$CuS\Theta_4 . 5H_2\Theta$

ition of sulphuric acid to form acid salts and double salts,
nposition of which the acid enters as $2SO_3$ or $4SO_3$, has
e chemists to regard the true formula of this acid as
r $H_2S_2O_5$ (or, if $S = 32$ and $\Theta = 16$, as $H_2S\Theta_4$), which
e two equivalents of potash to form a neutral salt, making
l a *bibasic* acid.

*osulphurous acid.**—This acid has not been obtained either
rous state or in combination with water, but as many salts
hich contain, in addition to a metallic oxide, sulphur and
e proportions expressed by the formula S_2O_2, many chemists
existence of hyposulphurous acid, having that composition,
which are therefore called *hyposulphites*.
ulphite of soda is by far the most important of these salts,
argely employed in photography, and as a substitute for

*Ὑπό, under, containing less oxygen than sulphurous acid.

sulphite of soda as an *antichlore*. The simplest method of preparing it consists in digesting powdered roll sulphur with solution of sulphite of soda ($NaO.SO_2$), when the latter dissolves an equivalent of sulphur and becomes hyposulphite of soda ($NaO.S_2O_2$), which crystallizes from the solution, when sufficiently evaporated, in fine prismatic crystals, having the formula $NaO.S_2O_2 + 5HO$.

On a large scale, the hyposulphite of soda is more economically prepared from the hyposulphite of lime obtained by exposing the refuse (*tank-waste* or *soda-waste*) of the alkali-works to the air for some days. This refuse contains a large proportion of sulphide of calcium, which becomes converted into hyposulphite of lime by oxidation—

$$2CaS + O_4 = CaO.S_2O_2 + CaO.$$

The hyposulphite of lime is dissolved out by water, and the solution mixed with carbonate of soda, when carbonate of lime is precipitated and hyposulphite of soda remains in solution—

$$CaO.S_2O_2 + NaO.CO_2 = CaO.CO_2 + NaO.S_2O_2.$$

The most remarkable and useful property of the hyposulphite of soda is that of dissolving the chloride and iodide of silver, which are insoluble in water and most other liquids.

On mixing a solution of nitrate of silver with one of chloride of sodium, a white precipitate of chloride of silver is obtained, the separation of which is much promoted by stirring the liquid; $AgO.NO_5 + NaCl = AgCl + NaO.NO_5$. The precipitate may be allowed to settle and washed twice or thrice by decantation. One portion of the chloride of silver is transferred to another glass, mixed with water, and solution of hyposulphite of soda added by degrees. The chloride of silver is very easily dissolved, yielding an intensely sweet solution, which contains the hyposulphite of silver, produced by double decomposition between the chloride of silver and hyposulphite of soda—

$AgCl$	+	$NaO.S_2O_2$	=	$NaCl$	+	$AgO.S_2O_2$.
Chloride of silver.		Hyposulphite of soda.		Chloride of sodium.		Hyposulphite of silver.

The hyposulphite of silver combines with the excess of hyposulphite of soda to form the double salt $AgO.S_2O_2.2(NaO.S_2O_2)$, which may be obtained in extremely sweet crystals from the solution.

If the other portion of the chloride of silver be exposed to the action of light, and especially of direct sunlight, it assumes by degrees a dark slate colour, from the formation of subchloride of silver, chlorine being set free; $2AgCl = Ag_2Cl + Cl$. By treating this darkened chloride of silver with hyposulphite of soda, as before, the unaltered chloride of silver will be entirely dissolved, but the subchloride will be decomposed into chloride of silver, which dissolves in the hyposulphite, and metallic silver, which is left in a very finely divided state as a black powder; $Ag_2Cl = AgCl + Ag$. The application of these facts in photography is well illustrated by the following experiments. A sheet of paper is soaked for a minute or two in a solution of 10 grains of common salt in an ounce of water contained in a flat dish. It is then dried, and soaked for three minutes in a solution of 50 grains of nitrate of silver in an ounce of water. The paper thus becomes impregnated with chloride of silver formed by the decomposition between the chloride of sodium and the nitrate of silver. It is now hung up in a dark place to dry. If a piece of lace, or a fern leaf, or an engraving on thin paper, with well-marked contrast of light and shade, be laid upon a sheet of the prepared paper, pressed down upon it by a plate of glass, and exposed for a short time to sunlight, a perfect representation of the object will be obtained, those parts of the sensitive paper to which the light had access having been darkened by the formation of subchloride of silver, whilst those parts which were protected from the light remain unchanged.

If this photographic print were again exposed to the action of light, it would be obliterated, the unaltered chloride of silver in the white parts being acted upon by light in its turn. The print is therefore fixed by soaking it for a short time

in a saturated solution of hyposulphite of soda, which dissolves the white unaltered chloride of silver entirely, and decomposes the subchloride formed by the action of light, leaving the black finely-divided metallic silver in the paper. The print should now be washed for two or three hours in a gentle stream of water, to remove all the hyposulphite of silver, when it will be quite permanent.

The power of hyposulphite of soda to dissolve chloride of silver has also been turned to account for extracting that metal from its ores, in which it is occasionally present in the form of chloride.

The behaviour of solution of hyposulphite of soda with powerful acids explains the circumstance that the hyposulphurous acid has not been isolated, for if the solution be mixed with a little diluted sulphuric or hydrochloric acid, it remains clear for a few seconds, and then becomes suddenly turbid from the separation of sulphur, at the same time evolving a powerful odour of sulphurous acid; $S_2O_2 = S + SO_2$. This disposition of the hyposulphurous acid to break up into sulphurous acid and sulphur also explains the precipitation of metallic sulphides, which often takes place when hyposulphite of soda is added to the acid solutions of the metals. Thus if an acid solution of chloride of antimony (obtained by boiling crude antimony ore (SbS_3) with hydrochloric acid) be added to a boiling solution of hyposulphite of soda, the sulphur separated from the hyposulphurous acid combines with the antimony to form a fine orange-red precipitate of sulphide of antimony (SbS_3), which is used in painting under the name of *antimony vermilion*. On the large scale the solution of hyposulphite of lime obtained from the alkali waste is employed in the preparation of antimony vermilion, as being less expensive than the soda-salt.

Instead of adding sulphur to sulphurous acid, hyposulphurous acid in combination may be obtained by removing oxygen from the former acid. Thus if an aqueous solution of sulphurous acid be acted on by zinc, one portion of the acid is deoxidised and converted into hyposulphurous acid, which combines with the oxide of zinc—

$$3SO_2 + Zn_2 = ZnO.SO_2 + ZnO.S_2O_2.$$

The presence of hyposulphite in the solution may be proved by adding hydrochloric acid.

When crystals of hyposulphite of soda are heated in the air, they first fuse in their water of crystallisation, then dry up to a white mass, which burns with a blue flame, leaving a residue of sulphate of soda. If heated out of contact with air, pentasulphide of sodium will be left with the sulphate of soda—

$$4(NaO.S_2O_2 + 5HO) = 20HO + 3(NaO.SO_3) + NaS_5.$$

None of the hyposulphites appear as yet to have been obtained in the perfectly anhydrous state, all of them retaining 1 eq. of water of constitution, which cannot be expelled without decomposition of the salt. Hence there is reason for believing that the elements of the water are really constituents of the hyposulphurous acid itself, and that instead of being expressed by the formula S_2O_2, it should be written HS_2O_3 ($= S_2O_2.HO$), the hyposulphite of soda being $NaO.HS_2O_3 + 4HO$, or $NaHS_2O_4 + 4HO$, instead of $NaO.S_2O_2 + 5HO$.

The *atomic formula* of the hyposulphite of soda would then be $Na_2H_2S_2\Theta_4 + 4H_2\Theta$ ($S = 32$, $\Theta = 16$).

150. *Hyposulphuric acid* or *dithionic acid* has not at present acquired any practical importance, and has not been obtained in the anhydrous state. To prepare a solution of the acid, binoxide of manganese in a state of fine division is suspended in

water and exposed to a current of sulphurous acid gas, the water being kept very cold whilst the gas is passing. A solution of hyposulphate of manganese is thus obtained; $2SO_2 + MnO_2 = MnO.S_2O_5$. Some sulphate of manganese is also formed at the same time; $SO_2 + MnO_2 = MnO.SO_3$, and if the temperature is allowed to rise, this will be produced in large quantity.

The solution containing sulphate and hyposulphate of manganese is decomposed by solution of baryta (baryta-water), when the oxide of manganese is precipitated together with sulphate of baryta, and hyposulphate of baryta is left in solution. From the filtered solution diluted sulphuric acid is carefully added until all the baryta is precipitated as sulphate of baryta, when the solution of hyposulphuric acid is filtered off and evaporated *in vacuo* over oil of vitriol. It forms a colourless fuming liquid, which is decomposed when heated into hydrated sulphuric and sulphurous acids; $HO.S_2O_5 = HO.SO_3 + SO_2$. Oxidising agents (nitric acid, chlorine, etc.) convert it into sulphuric acid.

The *hyposulphates* are not of any practical importance; they are all soluble, and are decomposed by heat, leaving sulphates, and evolving sulphurous acid.

151. *Trithionic acid*, or *sulphuretted hyposulphuric acid*, is also a practically unimportant acid, not known in the anhydrous state. Its hydrate is prepared from the trithionate of potash, which is formed by boiling a strong solution of bisulphite of potash with sulphur until the solution becomes colourless, and filtering the hot solution from any undissolved sulphur—

$$\underset{\text{Bisulphite of potash.}}{3(KO.HO.2SO_2)} + S = \underset{\text{Trithionate of potash.}}{2(KO.S_3O_5)} + KO.SO_3 + 3HO.$$

The solution deposits trithionate of potash in prismatic crystals. By dissolving these in water, and decomposing the solution with perchloric acid, the potash is precipitated as perchlorate, and a solution of trithionic acid is produced, from which the hydrated acid has been obtained in crystals. It is, however, very unstable, being easily resolved into sulphurous acid, sulphuric acid, and free sulphur—

$$HO.S_3O_5 = HO.SO_3 + SO_2 + S.$$

152. *Tetrathionic acid*, or *bisulphuretted hyposulphuric acid*, is rather more stable than the preceding acid, though equally devoid of practical importance. It is formed when hyposulphite of baryta, suspended in a little water, is treated with iodine, when tetrathionate of baryta is obtained in crystals—

$$\underset{\text{Hyposulphite of baryta.}}{2(BaO.S_2O_2)} + I = \underset{\text{Iodide of barium.}}{BaI} + \underset{\text{Tetrathionate of baryta.}}{BaO.S_4O_5}.$$

By exactly precipitating the baryta from a solution of the tetrathionate by addition of diluted sulphuric acid, the solution of tetrathionic acid may be obtained. When the solution is boiled, it is decomposed into sulphuric and sulphurous acids and free sulphur; $HO.S_4O_5 = HO.SO_3 + SO_2 + S_2$.

When solution of perchloride of iron is added to hyposulphite of soda, a fine purple colour is at first produced, which speedily vanishes, leaving a colourless solution. The purple colour appears to be due to the formation of the hyposulphite of sesquioxide of iron, which speedily decomposes, the ultimate result being expressed by the equation—

$$\underset{\text{Perchloride of iron.}}{Fe_2Cl_3} + \underset{\text{Hyposulphite of soda.}}{2(NaO.S_2O_2)} = \underset{\text{Tetrathionate of soda.}}{NaO.S_4O_5} + \underset{\text{Chloride of iron.}}{2FeCl} + \underset{\text{Chloride of sodium.}}{NaCl}.$$

153. *Pentathionic acid* possesses some interest as resulting from the action of sulphuretted hydrogen upon sulphurous acid, when much sulphur is deposited, and pentathionic acid remains in solution—

$$5HS + 5SO_2 = \underset{\text{Hydrated pentathionic acid.}}{HO.S_5O_5} + 4HO + S_5.$$

To obtain a concentrated solution of the acid, sulphuretted hydrogen and sulphurous acid are passed alternately through the same portion of water until a large deposition of sulphur has taken place. This is allowed some hours to settle; the clear liquid poured off and the solution concentrated by evaporation, first over a water-bath, and, finally, *in vacuo*, over oil of vitriol, for a concentrated solution. Pentathionic acid is decomposed by heat into sulphuric and sulphurous acids, with separation of sulphur; $HO.S_5O_5 = HO.SO_3 + SO_2 + S_3$.

Bisulphide of Carbon.

154. This very important compound (also called *bisulphuret of carbon*) is found in small quantity among the products of destructive distillation of coal, and is very largely manufactured for use as a solvent for sulphur, phosphorous, caoutchouc, fatty matters, &c. It is one of the few compounds of carbon which can be obtained by the direct union of their elements, and is prepared by passing vapour of sulphur over charcoal heated to redness.

In small quantity bisulphide of carbon is easily prepared in a tube of German glass (combustion-tube) about two feet long and half-an-inch in diameter (fig. 195). This tube is closed at one end, and a few fragments of sulphur dropped into it, so as to occupy two or three inches. The rest of the tube is filled up with small frag-

Fig. 195.

ments of recently calcined wood charcoal. The tube is placed in a combustion-furnace, and its open end connected by a perforated cork with a glass tube, which dips just below the surface of water contained in a bottle placed in a vessel of very cold water. That part of the tube which contains the charcoal is first surrounded with red-hot charcoal, and when it is heated to redness, a little red-hot charcoal is placed near the end containing the sulphur (hitherto protected by a sheet-iron screen), so that the vapour of sulphur may be slowly passed over the red-hot charcoal. The bisulphide of carbon being insoluble in water, and much heavier (sp. gr. 1·27), is deposited beneath the water in the receiver. To purify the bisulphide of carbon from the water and the excess of sulphur which is deposited with it, the water is carefully drawn off with a small syphon, the bisulphide of carbon transferred to a flask, and a few fragments of chloride of calcium dropped into it to absorb the water. A bent tube connected with a Liebig's condenser, or with a worm, is attached to the flask (fig. 196) by a perforated cork, and the flask is gently heated in a water bath, when the bisulphide of carbon is distilled over as a perfectly colourless liquid. The inflammability of the bisulphide of carbon renders great care necessary.

Fig. 196.

On a large scale, a fire-clay retort is filled with fragments of charcoal and heated to redness, pieces of sulphur being occasionally dropped in through an earthenware tube passing to the bottom of the retort. When very large quantities are made, coke is employed, and the vapour of sulphur is obtained from iron pyrites.

The bisulphide of carbon is possessed of some very remarkable properties: it is a very brilliant liquid, the light passing through which is partly decomposed into its component coloured rays before it reaches the eye. *These properties are dependent upon its high* refractive and dispersive

powers, which are turned to great advantage in optical experiments, esp... cially in *spectrum analysis*, where the rays emanating from a colou... flame are analysed by passing them through a prismatic bottle filled w... bisulphide of carbon. It is also highly *diathermanous*, that is, it a... rays of heat to pass through it with comparatively little loss, so that ... be rendered opaque to light by dissolving iodine in it, the rays of l... emanating from a luminous object may be arrested, whilst the calo... rays are allowed to pass. It has never been frozen, and is there... employed in thermometers for measuring very low temperatures. Bi... phide of carbon is a very volatile liquid, readily assuming the form... vapour at the ordinary temperature, and boiling at 118°·5 F. Its vap... when diluted with air, has a very disgusting and exaggerated odour... sulphuretted hydrogen, but the smell at the mouth of the bottle is ethe... and not unpleasant.

The rapid evaporation of bisulphide of carbon is, of course, productive of gr... cold. If a few drops be placed in a watch-glass and blown upon, they soon pass... in vapour, and the temperature of the glass is so reduced that the moisture of t... breath condenses upon it in hoar-frost, which melts when the glass is placed in t... palm of the hand. If a glass plate be covered with water, a watch-glass contain... bisulphide of carbon placed on it, and evaporation promoted by blowing through... tube, the watch-glass will be frozen on to the plate, so that the latter may be li... up by it.

The bisulphide of carbon is exceedingly inflammable; it takes fire at a... temperature far below that required to inflame ordinary combustible... bodies, and burns with a bright blue flame, producing carbonic and sul... phurous acids ($CS_2 + O_6 = CO_2 + 2SO_2$), and having a great tendency t... deposit sulphur unless the supply of air is very good.

If a little bisulphide of carbon be dropped into a small beaker, it may be inflamed... by holding in its vapour a test-tube containing oil heated to about 300° F., which... will be found incapable of firing gunpowder or of inflaming any ordinary com... bustible substance. An iron rod heated below redness will be found quite incap... able of firing the explosive mixture of hydrogen or coal-gas with oxygen (fig. 197),... but if the cylinder be placed upon a glass... plate, on which is laid a piece of paper soaked... in bisulphide of carbon, and allowed to stand... for a few moments, it will be found that the... same rod will afterwards inflame the mixture,... even although a little cooler than before. If... a little bisulphide of carbon be dropped into a... *strong* cylinder of oxygen, a mixture will be... formed which explodes with great noise on the... approach of a flame.

Fig. 197.

Since vapour of bisulphide of carbon is liable to be present in coal-gas, its great inflammability has been cited to account for explosions produced by sparks from workmen's tools against the pavement, which would be incapable of inflaming pure coal-gas.

The abundance of sulphur separated in the flame of bisulphide of carbon enables it to burn iron by converting it into sulphide. If some bisulphide of carbon be boiled in a test-tube provided with a piece of glass tube from which the vapour may be burnt, and a piece of thin iron wire be held in the flame (fig. 198), it will burn with vivid scintillation, the fusible sulphide of iron dropping off.

The vapour of bisulphide of carbon acts very injuriously if breathed for ... length of time, producing symptoms somewhat resembling those ... l by sulphuretted hydrogen. Its poisonous properties have been ... to account for killing insects in grain without injuring it.

The chief applications of bisulphide of carbon depend upon its power of solving the oils and fats. After as much oil as possible has been extracted from seeds and fruits by pressure, fresh quantity is obtained by treating the pressed cake with bisulphide of carbon, which is afterwards recovered by distillation from the oil. In Algiers bisulphide of carbon is employed for extracting the essential oils in which reside the perfumes of roses, jasmine, lavender, &c.

Fig. 198.

Bisulphide of carbon has often been made a starting point in the attempts to reproduce organic compounds by synthesis. It may be employed in the formation of the hydrocarbons which are usually derived from organic sources, for if it be mixed with sulphuretted hydrogen (by passing the gas through a bottle containing bisulphide of carbon gently warmed), and passed over copper-turnings heated to redness in a porcelain tube, olefiant gas will be produced—

$$4CS_2 + 4HS + Cu_{12} = 12CuS + C_4H_4 .$$

The action of bisulphide of carbon upon ammonia is practically important for the easy production of *sulphocyanide of ammonium*, which is formed when the bisulphide of carbon is dissolved in alcohol, and acted on by ammonia with the aid of heat—

$$\underset{\text{Bisulphide of carbon.}}{2CS_2} + 2NH_3 = 2HS + \underset{\text{Sulphocyanide of ammonium.}}{NH_3 . HC_2NS_2} .$$

Bisulphide of carbon is the sulphur-acid corresponding to carbonic acid, and is often called sulphocarbonic acid; it combines with some of the sulphur-bases to form *sulphocarbonates*, which correspond to the carbonates, containing sulphur in place of oxygen. Thus, when a solution of sulphide of potassium in alcohol is mixed with bisulphide of carbon, the sulphocarbonate of (sulphide of) potassium is deposited in orange-yellow crystals. Even the hydrogen compound corresponding in composition to the unknown hydrate of carbonic acid may be obtained as a yellow oily liquid by decomposing sulphocarbonate of potassium with hydrochloric acid—

$$\underset{\substack{\text{Sulphocarbonate}\\ \text{of potassium.}}}{KS . CS_2} + HCl = \underset{\substack{\text{Hydrosulphocarbonic}\\ \text{acid.}}}{HS . CS_2} + KCl .$$

As would be expected, the sulphocarbonates, when boiled with water, exchange their sulphur for oxygen, becoming carbonates—

$$KS . CS_2 + 3HO = KO . CO_2 + 3HS .$$

The bisulphide of carbon vapour in coal-gas is one of the most injurious of the impurities, and one of the most difficult to remove with economy. It is especially injurious, because when burning in the presence of aqueous vapour, a part of its sulphur is converted into sulphuric acid, the corrosive effects of which are so damaging. Several processes have been devised for its removal. The gas has been washed with the *ammoniacal liquor (containing hydrosulphate of ammonia)* which absorbs the bisul-

phide. Steam, at a high temperature, has been employed to convert it into hydrosulphuric and carbonic acids, which are both easily removed from the gas; $CS_2 + 2HO = CO_2 + 2HS$. Lime at a red heat decomposes it in a similar way; $CS_2 + 3CaO = CaO.CO_2 + 2CaS$. Oxide of lead dissolved in caustic soda has been used to convert it into sulphide of lead; $CS_2 + 2PbO + NaO = 2PbS + NaO.CO_2$. Its removal as sulphocarbonate by an alcoholic solution of potash or soda has also been proposed. At present, however, it retains its character as one of the most troublesome impurities with which the gas manufacturer has to deal.

Composition of bisulphide of carbon.—Analysis proves that 6 parts by weight (1 eq.) of carbon are combined with 32 parts (2 eqs.) of sulphur in the bisulphide, and since 1 equivalent of sulphide of potassium (55 parts) is combined with 38 parts of bisulphide in the sulphocarbonate, the formula CS_2 is taken to represent 1 equivalent of the bisulphide of carbon. The specific gravity, or weight of 1 volume of bisulphide of carbon vapour, is 2·6447. Supposing, then, 1 equivalent (8 parts) of oxygen to occupy 1 volume, 1 equivalent (38 parts) of bisulphide would occupy 2 volumes—

	Specific gravity.	
2 volumes of CS_2 vapour weigh	(2·6447 × 2)	5·2894
2 volumes (2 equivalents) of sulphur vapour	(2·23 × 2)	4·4600
		·8294

The difference represents the weight of imaginary carbon vapour contained in 2 volumes of vapour of bisulphide of carbon; this weight of imaginary carbon vapour was assumed, on the grounds set forth at p. 81, to occupy 2 volumes.

Hence, 1 equivalent, or 2 volumes of bisulphide of carbon vapour, contains 1 equivalent or 2 volumes of imaginary carbon vapour, combined with 2 equivalents or 2 volumes of sulphur vapour, its composition by volume being precisely analogous to that of carbonic acid. The *molecular formula* of bisulphide of carbon would be ΘS_2 (Θ = 12, S = 32), representing 2 volumes (H = 1 volume).

155. *Bisulphide of silicon* (SiS_2), corresponding in composition to bisulphide of carbon, is obtained by burning silicon in sulphur vapour, or by passing vapour of bisulphide of carbon over a mixture of silica and charcoal. Unlike the carbon compound, it is a white amorphous solid, absorbing moisture when exposed to air, and soluble in water, which gradually decomposes it into silicic and hydrosulphuric acids—

$$SiS_2 + 2HO = SiO_2 + 2HS.$$

When heated in air, it burns slowly, yielding silicic and sulphurous acids.

156. *Bisulphide of nitrogen* (NS_2) is a yellow crystalline explosive substance, produced by a complicated reaction which takes place when chloride of sulphur, dissolved in bisulphide of carbon, is acted on by gaseous ammonia, when hydrochlorate of ammonia is deposited, and the filtered liquid, allowed to evaporate, deposits bisulphide of nitrogen mixed with sulphur, which may be dissolved out by bisulphide of carbon, in which the nitrogen compound is nearly insoluble; this substance is remarkable for its sparing solubility, its irritating odour, and its explosibility when struck or moderately heated, its elements being held together by a very feeble attraction.

157. CHLORIDES OF SULPHUR.—The *subchloride*, or *dichloride of sulphur* (S_2Cl), is the most important of these, since it is employed in the process of vulcanising caoutchouc. It is very easily prepared by passing dry chlorine over sulphur very gently heated in a retort (fig. 199); the sulphur quickly melts, and the dichloride of sulphur distils over into the

ver as a yellow volatile liquid (boiling point, 280° F.), which has a
peculiar odour. It fumes strongly in air, the moisture decomposing

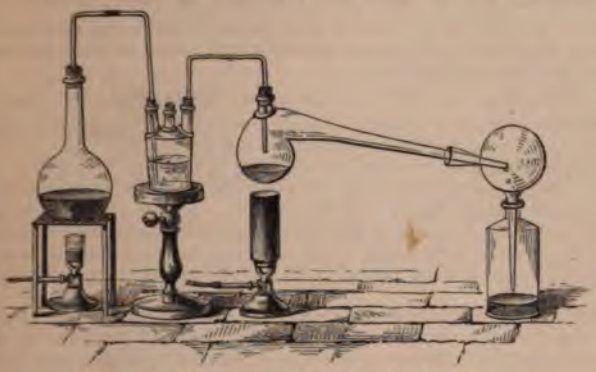


Fig. 199.—Preparation of subchloride of sulphur.

rming hydrochloric and sulphurous acids, and causing a deposit of
ur upon the neck of the bottle—

$$2S_2Cl + 2HO = 2HCl + SO_2 + S_3 .$$

n poured into water, it sinks (sp. gr. 1·68) and slowly undergoes de-
position; the separated sulphur, of course, belongs to the electroposi-
variety (see p. 187), and the solution contains, beside hydrochloric
sulphurous acids, some of the acids containing a larger proportion of
hur. The specific gravity of the vapour of dichloride of sulphur is
showing that it contains 2 vols. Cl (4·94) and 2 vols. S (4·46), con-
ed into 2 vols. (9·40) of vapour of dichloride of sulphur. Its *mole-
r formula* would therefore be S_2Cl_2(S = 32), representing 2 vols.
= 1 vol.)

loride of sulphur (SCl) is a far less stable compound than the dichloride, from
h it is obtained by the action of an excess of chlorine. It is a dark red fuming
d, easily resolved, even by sunlight, into free chlorine and dichloride of sulphur.
ide of sulphur (SI) is a crystalline unstable substance, produced by the direct
n of its elements, and occasionally employed in medicine.
biodide of sulphur, or *bisulphide of iodine* (S_2I), is obtained in large tabular
als resembling iodine, by decomposing the subchloride of sulphur with iodide
byle: $S_2Cl + C_4H_9I = S_2I + C_4H_9Cl$.

Selenium.—Eq. 39·75.

3. Selenium (Σελήνη, *the moon*) is a rare element, very closely allied to sulphur
natural history, physical characters, and chemical relations to other bodies.
found sparingly in the free state associated with some varieties of native sul-
but more commonly in combination with metals, forming *selenides*, which are
l together with the sulphides. The iron pyrites of Fahlun, in Sweden, is
ially remarkable for the presence of selenium, and was the source whence this
ent was first obtained. The Fahlun pyrites is employed for the manufacture
of vitriol, and in the leaden chambers a reddish brown deposit is found, which
nalysed by Berzelius in 1817, and found to contain the new element.
order to extract selenium from the seleniferous deposit of the vitriol works, it
be boiled with sulphuric acid diluted with an equal volume of water, and nitric
added in small portions until the oxidation is completed, when no more red
s will escape. The solution, containing selenious (SeO_2) and selenic (SeO_3)
is largely diluted with water, filtered off from the undissolved matters, mixed

with about one-fourth of its bulk of hydrochloric acid, and somewhat concentrated by evaporation, when the hydrochloric acid reduces the selenic to selenious acid—

$$HO.SeO_3 + HCl = HO.SeO_2 + HO + Cl.$$

A current of sulphurous acid gas is now passed through the solution, when the selenium is precipitated in fine red flakes, which collect into a dense black mass when the liquid is gently heated—

$$HO.SeO_2 + HO + 2SO_2 = 2(HO.SO_3) + Se.$$

The proportion of selenium in the deposit from the leaden chambers is variable. The author has obtained above 8 per cent. by this process.

Selenium, like sulphur, is capable of existing in three allotropic states: the amorphous variety precipitated from its solutions, or sublimed like flowers of sulphur; the black vitreous form; and the crystalline form deposited from its solution in bisulphide of carbon, in which it is far less easily dissolved than sulphur. When heated, it fuses easily, boils below a red heat, and is converted into a deep yellow vapour, which expands when heated in the same anomalous manner as vapour of sulphur.

Selenium is less combustible than sulphur; when heated in air it burns with a blue flame, and emits a peculiar odour like that of putrid horse-radish, which appears to be due to the formation of a little selenietted hydrogen from the moisture of the air. When heated with oil of vitriol, selenium forms a green solution which deposits the selenium again when poured into water.

Selenious acid (SeO_2), corresponding to sulphurous acid, is the product of combustion of selenium in oxygen. It is best obtained by dissolving selenium in boiling nitric acid (which would convert sulphur into sulphuric acid), and evaporating to dryness, when the selenious acid remains as a white solid which sublimes in needle-like crystals when heated. When dissolved in boiling water, it yields a crystalline hydrate of selenious acid.

Selenic acid (SeO_3) is not known in the anhydrous state. It is formed when selenium is oxidised by fused nitre; $KO.NO_5 + Se = KO.SeO_3 + NO_2$. By dissolving the seleniate of potash in water, and adding nitrate of lead, a precipitate of seleniate of lead ($PbO.SeO_3$) is obtained, and if this be suspended in water and decomposed by passing hydrosulphuric acid gas, lead will be removed as insoluble sulphide, and a solution of hydrated selenic acid will be obtained—

$$PbO.SeO_3 + HS = HO.SeO_3 + PbS.$$

This solution may be evaporated till it has a sp. gr. of 2·6, when it very closely resembles oil of vitriol. It is decomposed, however, at about 550° F., evolving oxygen, and becoming selenious acid. It oxidises the metals like oil of vitriol, and even dissolves gold. The seleniates closely resemble the sulphates, but they are decomposed when heated with hydrochloric acid, chlorine being evolved, and selenious acid produced.

Hydroselenic acid, or *selenietted hydrogen* (HSe), is the exact parallel of sulphuretted hydrogen, and is produced by a similar process. It is even more offensive and poisonous than that gas, and acts in a similar way upon metallic solutions, precipitating the *selenides*.

There are two *chlorides of selenium*: the dichloride, Se_2Cl, a brown volatile liquid corresponding to dichloride of sulphur; and the bichloride, $SeCl_2$, a white crystalline solid, without any well-established analogue in the sulphur series.

Notwithstanding the resemblance between the two elements, there are two *sulphides of selenium*, a bisulphide (SeS_2) and a tersulphide (SeS_3). The former is obtained as a yellow precipitate when hydrosulphuric acid is passed into solution of selenious acid.

TELLURIUM.—Eq. 64·5.

159. Tellurium (from *tellus, the earth*) is connected with selenium by analogies stronger than those which connect that element with sulphur. It is even less frequently met with than selenium, being found chiefly in certain Transylvanian gold ores. It occasionally occurs in an uncombined form, but more frequently in combination with metals. Foliated or *graphic tellurium* is a black mineral containing tellurides of lead, silver, and gold. Telluride of bismuth is also found in nature.

ellurium is extracted from the foliated ore by a process similar to that for ob-
ing selenium. From telluride of bismuth it is procured by strongly heating the
with a mixture of carbonate of potash and charcoal, when telluride of potassium
rmed, which dissolves in water to a purple-red solution, from which tellurium is
sited on exposure to air.

'ellurium much more nearly resembles the metals than the non-metals in its
sical properties, and is on that account often classed among the former, but it is
capable of forming a basic oxide. In appearance it is very similar to bismuth
th which it is so frequently found), having a pinkish metallic lustre, and being,
that metal, crystalline and brittle. It fuses below a red heat, and is converted
a yellow vapour at a higher temperature. When heated in air it burns with a
e flame edged with green, and emits fumes of tellurous acid (TeO_2) and a peculiar
or.

ike selenium, tellurium is dissolved by strong sulphuric acid, yielding a purple-
olution, from which water precipitates it unchanged.

he *oxides of tellurium* correspond in composition to those of selenium. *Tellurous*
(TeO_2) is precipitated in the hydrated state when a solution of tellurium in
ed nitric acid is poured into water. If the nitric solution is boiled, a crystal-
precipitate of anhydrous tellurous acid is obtained. Unlike selenious acid,
rous acid is sparingly soluble in water. It is easily fusible, forming a yellow
, which becomes white on cooling, and it may be sublimed unchanged. Its acid
acter is rather feeble, and with some of the stronger acids, it forms soluble
pounds in which it takes the part of a very feeble base.

elluric acid (TeO_3) is also a weak acid obtained by oxidising tellurium with nitre,
ipitating the tellurate of potash with chloride of barium, and decomposing the
rate of baryta with sulphuric acid. On evaporating the solution, crystals of
ated telluric acid ($HO.TeO_3 + 2HO$) are obtained, which become $HO.TeO_3$ at
derate heat, and when heated nearly to redness, are converted into an orange-
w powder, which is the anhydrous acid. In this state it is insoluble in acids and
lies. When strongly heated, it evolves oxygen, and becomes tellurous acid.
tellurates are unstable salts which are converted into tellurites when heated.

'elluretted hydrogen, or *hydrotelluric acid* (HTe), exhibits in the strongest manner
chemical analogy of tellurium with selenium and sulphur. It is a gas very
lar to sulphuretted hydrogen in smell, and in most of its other properties.
en its aqueous solution is exposed to the air, it yields a brown deposit of tellu-
n. When passed into metallic solutions it precipitates the tellurides.

he gas is prepared by decomposing telluride of zinc with hydrochloric acid.

he most characteristic property of tellurium compounds, is that of furnishing
purple solution of telluride of potassium, when fused with carbonate of potash
charcoal, and treated with water. Two solid *chlorides of tellurium* have been
ined; TeCl is a black solid with a violet coloured vapour, and is decomposed by
r into tellurium and $TeCl_2$. The latter may be obtained as a white crystalline
tile solid, decomposed by much water into hydrochloric and tellurous acids.
re are also two *sulphides of tellurium* corresponding to the oxides, from which
may be obtained as dark brown precipitates, by the action of hydrosulphuric
. They are both sulphur-acids, and, therefore, soluble in alkaline sulphides.

60. *Review of the sulphur group of elements.*—The three elements—
hur, selenium, and tellurium—exhibit a relation of a similar character
hat observed between the members of the chlorine group, both in their
sical and chemical properties.

ulphur is a pale yellow solid, easily fusible and volatile, without any
e of metallic lustre, and of specific gravity 2·05 (sp. gr. of vapour,
). Selenium is either a red powder or a lustrous mass appearing
k, but transmitting red light through thin layers, much less fusible
volatile than sulphur, and of specific gravity 4·8 (sp. gr. of vapour,
). Tellurium has a brilliant metallic lustre, is much less fusible and
tile than selenium, and of specific gravity 6·65 (sp. gr. of vapour, 9·0).
ulphur (eq. 16) has the most powerful attraction for oxygen, hydro-
, and the metals. Selenium (eq. 39·75) ranks next in the order of
nical energy. Tellurium (eq. 64·5) has a less powerful attraction for

oxygen, hydrogen, and the metals, than either sulphur or selenium. element appears to stand on neutral ground between the non-me bodies and the less electropositive metals.

PHOSPHORUS.

161. This is the only element for the ordinary preparation of w animal substances are employed. It is never known to occur uncom in nature, but is found abundantly in the form of *phosphate of* ($3CaO . PO_5$), which is contained in the minerals *coprolite*, *phosph* and *apatite*, and occurs diffused, though generally in small propo through all soils upon which plants will grow, for this substance essential constituent of the food of most plants, and especially o cereal plants which form so large a proportion of the food of an The seeds of such plants are especially rich in the phosphates of lim magnesia.

Animals feeding upon these plants still further accumulate the phoric acid, for it enters, chiefly in the form of phosphate of lime, in composition of almost every solid and liquid in the animal body, especially abundant in the bones, which contain about three-fift their weight of phosphate of lime. It is from this source that our s of phosphorus is chiefly derived.

Composition of the Bones of Oxen.

Animal matter, ...	30·58
Phosphate of lime, ...	57·67
Fluoride of calcium, ...	2·69
Carbonate of lime, ...	6·99
Phosphate of magnesia, ...	2·07
	100·00

What is here termed animal matter is a cartilaginous substan verted into gelatine when the bones are heated with water under p and containing carbon, hydrogen, nitrogen, and oxygen. It was f the custom to get rid of this by burning the bones in an open f the increased demand for chemical products, and the diminished of bones, have taught economy, so that the cartilaginous matter dissolved out by heating the bones with water at a high pressure manufacture of glue; or the bones are subjected to destructive tion, so as to save the ammonia which they evolve, and the bone thus produced is used by the sugar-refiner until its decolorising are exhausted, when it is heated in contact with air to burn a charcoal, and leave the *bone-ash*, consisting chiefly of phosphate ($3CaO . PO_5$). In order to extract the phosphorus, the bone-ash is for some time with diluted sulphuric acid, which removes the grea of the lime in the form of the sparingly soluble sulphate of lime, the phosphoric acid in the solution, which is strained from the evaporated to a syrup, mixed with charcoal, thoroughly dried in pot, and distilled in an earthen retort (fig. 200), when the carbon r the oxygen from the phosphoric acid, and the phosphorus distil and is condensed in a receiver containing water to protect it f

of the air. The decomposition of the dried phosphoric acid by the
n of the charcoal is expressed by the equation—

$$\underset{\text{Hydrated phosphoric acid.}}{HO.PO_5} + C_6 = \underset{\text{Carbonic oxide.}}{6CO} + H + P.$$

s is the simplest account that can be given of the preparation of phosphorus
one-ash, but it is not strictly correct, for the sulphuric acid does not remove

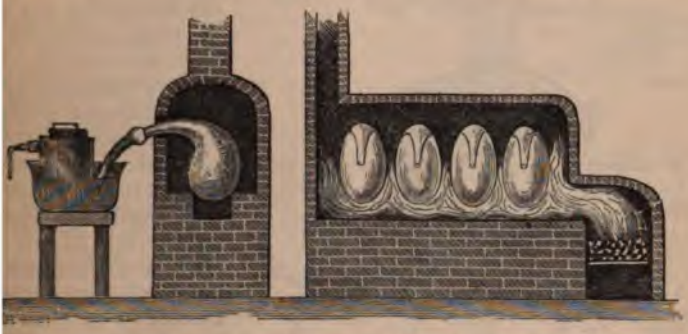


Fig. 200.—Extraction of phosphorus.

hole of the lime from the phosphate, a portion remaining in the solution con-
ng the phosphoric acid, so that this solution is generally said to contain *super-
hate of lime*, and the action of the sulphuric acid is thus represented—

$$\underset{\text{Bone phosphate of lime.}}{3CaO.PO_5} + 2(HO.SO_3) = \underset{\text{Superphosphate of lime.}}{CaO.2HO.PO_5} + 2(CaO.SO_3).$$

hen the superphosphate of lime is dried, it becomes converted into *metaphos-
of lime* ($CaO.PO_5$), and on distilling this with charcoal—

$$\underset{\text{Metaphosphate of lime.}}{3(CaO.PO_5)} + C_{10} = \underset{\text{Bone phosphate of lime.}}{3CaO.PO_5} + 10CO + P_2.$$

icic acid (sand) is sometimes added to combine with the lime, and liberate the
inder of the phosphoric acid, so that it may be decomposed by the charcoal.
the small scale, for the sake of illustration, phosphorus may be prepared by a
ss which has also been successfully employed for its manufacture in quantity,
onsists in heating a mixture of bone-ash and charcoal in a stream of hydro-
ic acid gas—

$$CaO.PO_5 + 3HCl + C_8 = 3CaCl + 8CO + H_3 + P.$$

mixture of equal weights of well-dried charcoal and bone-ash, both in fine
er, is introduced into a porcelain tube sheathed with copper, and placed in a
oal furnace (fig. 201). One end of the tube is connected with a flask (A), con-
ng fused salt and sulphuric acid for evolving hydrochloric acid, and the other is
nted with putty into a bent retort-neck (B), for conveying the phosphorus
a vessel of water (C). On heating the porcelain tube to bright redness, phos-
is distils over in abundance. The hydrogen and carbonic oxide inflame as
escape into the air, from their containing phosphorus vapour.

hen first prepared the phosphorus is red and opaque, from the pre-
e of some suboxide of phosphorus and mechanical impurities; the
r are removed by melting the phosphorus under warm water, and
ezing it through wash leather. The phosphorus is then fused under
onia to remove any acid impurity, and afterwards under bichromate

of potash acidified with sulphuric acid, when the chromic acid oxidises the suboxide of phosphorus, and converts it into phosphoric acid which dissolves. The phosphorus is then thoroughly washed, melted under water, and drawn up into glass tubes, where it solidifies into the sticks in which it is sold. These are always preserved under water from the action of oxygen, and in tin cases from that of light.

Fig. 201.

Pure ordinary phosphorus is almost colourless and transparent, but when exposed to light, and especially to direct sun-light, it gradually acquires an opaque red colour, from its partial conversion into the allotropic variety known as red or *amorphous phosphorus*. By tying bands of black cloth round a stick of phosphorus and exposing it, under water, to the action of sun-light, alternate zones of red may be produced.

Even though the phosphorus be screened from light, it will not remain unchanged unless the water be kept quite free from air, which irregularly corrodes the surface of the phosphorus, rendering it white and opaque. This action is accelerated by exposure to light.

The most remarkable character of ordinary phosphorus is its easy inflammability. It inevitably takes fire in air when heated a little above its melting point (111°·5 F.), burning with a brilliant white flame, which becomes insupportable when the combustion takes place in oxygen (p. 6), and evolving dense white clouds of solid phosphoric acid. When a piece of dry phosphorus is exposed to the air, it combines slowly with oxygen, forming phosphorous acid,* and its temperature often becomes so much elevated during this slow combustion, that it melts and takes fire, especially if the combination be encouraged by the warmth of the hand or by friction. Hence, ordinary phosphorus must never be handled or cut in the dry state, but always under water, for it causes most painful burns.

The slow oxidation of phosphorus is attended with that peculiar luminous appearance which is termed *phosphorescence* (φῶς, *light*, φέρω, *to bear*), but this glow is not seen in pure oxygen or in air containing a minute proportion of olefiant gas or oil of turpentine. It will be remembered that the slow oxidation of phosphorus is attended with the formation of ozone.

* The white fumes evolved by phosphorus in moist air are said to consist partly of trite of ammonia, formed by the action of the ozonised oxygen upon the air and aqueous pour.

aracteristic behaviour of phosphorus in air is best observed when the phos- in a finely-divided state. When a fragment of phosphorus is shaken with sulphide of carbon, it is quickly dissolved, and if the solution be poured iece of filtering-paper (fig. 202), and allowed to evaporate in a darkened very thin film of phosphorus left will exhibit a glow increas- lliancy till the phosphorus bursts pontaneous combustion.

Fig. 202.

phorus be dissolved in olive oil, e heat, the solution is strongly scent when shaken in a bottle g air, or when rubbed upon the

ters may be written on paper tick of phosphorus held in a dded piece of damp paper (hav- sel of water at hand into which to plunge the phosphorus if it should . When the paper is held with its back to the fire, or to a hot iron, ened room, a twinkling combustion of the finely-divided phosphorus will d the letters will be burnt into the paper. Phosphorus, which has been idised, is even more easily inflamed than pure phosphorus. If a few small phosphorus be placed in a dry stoppered bottle, gently warmed till they then shaken round the sides of the bottle so as to become partly converted oxide of phosphorus, it will be found, long after the bottle is cold, to be ously inflammable, so that if a wooden match tipped with sulphur be rubbed , the phosphorus which it takes up will ignite when the match is brought air, kindling the sulphur, which will inflame the wood. This was one of st forms in which phosphorus was employed for the purpose of procuring taneous light. If the stopper be greased, the phosphorus may be preserved d for a long time.

last experiment, if the wood had not been tipped with sulphur, the phos- ould not have kindled it, the flame of phosphorus generally being unable solid combustibles, because it deposits upon them a coating of phosphoric ch protects them from the action of air. Hence, in the manufacture of atches, the wood is first tipped with sulphur, or wax, or paraffine, which e off combustible vapours to be kindled by the flame of the phosphorus on, and thus to inflame the wood.

all stick of phosphorus be carefully dried with filtering paper, and dropped nder of oxygen, which is afterwards covered with a glass plate, no luminosity served in a darkened room until the cylin- ced under the air-pump receiver, and the exhausted. When the oxygen has thus been about one-fifth of its former density, the escence will be seen. A similar effect may ed by covering the cylinder of oxygen con- he phosphorus (having removed the glass th another cylinder, about four times its 203), filled with carbonic acid, which will dilute the oxygen and produce phosphor- By suspending—in a bottle of air contain- ngly luminous piece of phosphorus—a piece with a drop of oil of turpentine upon it, the be almost instantaneously destroyed. A e of olefiant gas or coal-gas dropped into will also extinguish the luminosity.

Fig. 203.

ary phosphorus is slowly converted into vapour at the ordinary ture, and emits in the air white fumes with a peculiar alliaceous hich appear phosphorescent in the dark. When heated out of with air, it boils at 550° F., and is converted into a colourless

minosity of phosphorus vapour is seen to advantage when a piece of phos- *boiled with water in a narrow-necked* flask, or a test-tube with a cork and

narrow tube. The steam charged with vapour of phosphorus has all the a of a blue flame in a darkened room, but of course combustibles are not in it, since its temperature is not higher than 212° F. Phosphorus may b with perfect safety in an atmosphere of carbonic acid, the neck of the r allowed to dip under water in the receiver.

Although ordinary phosphorus is of a decidedly glassy or vitre ture, and not at all crystalline, it may be obtained in dod crystals, by allowing its solution in bisulphide of carbon to ev an atmosphere of carbonic acid.

The conversion of ordinary phosphorus into the red or *amorp phorus* is one of the most striking instances of allotropic mo When phosphorus is heated for a considerable length of time 450° F. *in vacuo*, or in an atmosphere in which it cannot burn, i converted into a red infusible mass of amorphous phosphorus. of phosphorus differs as widely from the vitreous form as graph from diamond. It is almost unchangeable in the air, evolves n is not luminous, cannot be inflamed by friction, or even by any l of 500° F., when it actually becomes reconverted into ordinary pho Amorphous phosphorus is insoluble in the solvents for ordinary ph The two varieties also differ greatly in specific gravity, that of th phosphorus being 1·83, and of the amorphous variety 2·14.

The conversion of vitreous into amorphous phosphorus may be effected it in a flask (A, fig. 204) placed in an oil-bath (B), maintained at a te ranging from 450° to 460° F., the flask being furnished with a bent tube (into mercury, and with an (D) for supplying carboni dried by passing over chlo cium. The flask should be f filled with carbonic acid be ing heat, and the tube de may then be closed with a s (E). After exposure to hea forty hours, but little ordi phorus will remain, and th removed by allowing the remain in contact with bi carbon for some hours, quently washing it with phide of carbon till the la no phosphorus when evapo

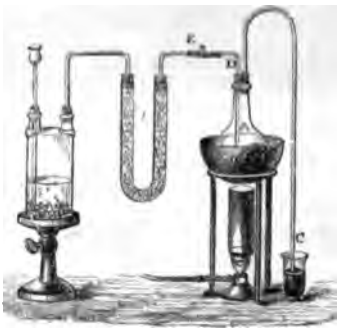


Fig. 204.

On the large scale, the phorus is prepared by hea 200 lbs. of vitreous pho 450° F. in an iron boiler. After three or four weeks the phosphorus is converted into a hard red brittle mass, which is ground by mill-stones u and separated from the ordinary phosphorus either by bisulphide of carbo soda, in which the latter is soluble. The temperature requires care tion, for if it be allowed to rise to 500°, the red phosphorus quickly r vitreous condition, evolving the heat which it had absorbed during its and thus converting much of the phosphorus into vapour. This reconv be shown by heating a little red phosphorus in a narrow test-tube, wh vitreous phosphorus condense on the cool part of the tube. The colour specimens of amorphous phosphorus varies considerably; that prepa large scale is usually of a dark purplish colour, but it may be obtained scarlet colour. Rhombohedral crystals of phosphorus, resembling crystal in form and metallic appearance, have been obtained by fusing phosp lead, and dissolving out the latter with diluted nitric acid (sp. gr. 1·1).

* According to Hittorf, the reconversion does not take place till 800° F., t us being convertible into vapour below that temperature, without fusion.

dinary phosphorus is very poisonous, whilst amorphous phosphorus rs to be harmless. The former is employed, mixed with fatty sub- es, for poisoning rats and beetles. Cases are, unhappily, not very of children being poisoned by sucking the phosphorus composition ucifer matches. The vapour of phosphorus also produces a very ous effect upon the persons engaged in the manufacture of lucifer hes, resulting in the decay of the lower jaw-bone. This evil is much ated by good ventilation, or by diffusing turpentine vapour through ir of the work-room, and attempts have been made to obviate it ely by substituting amorphous phosphorus for the ordinary variety, as might be expected, the matches thus made are not so sensitive to on as those in which the vitreous phosphorus is used.

he difference between the two varieties of phosphorus, in respect to nical energy, is seen when they are placed in contact with a little he on a plate, when the ordinary phosphorus undergoes combustion, the red phosphorus remains unaltered.

Black phosphorus has been obtained by heating vitreous phosphorus to tle above its melting point and suddenly cooling it. It is reconverted fusion and slow cooling. *Viscous phosphorus* results from the sudden ing of phosphorus heated nearly to its boiling point.

rdinary phosphorus is capable of direct union with oxygen, chlorine, mine, iodine, sulphur, and most of the metals, with which it forms *phides* or *phosphurets*. Even gold and platinum unite with this ent when heated, so that crucibles of these metals are liable to cor- n when heated in contact with a phosphate in the presence of a ing agent, such as carbon. Thus the inside of a platinum dish or ble is roughened when vegetable or animal substances containing phates are incinerated in it. The presence even of small quantities osphorus in metallic iron or copper produces considerable effect upon physical qualities.

osphorus has the property, a very remarkable one in a non-metal, of pitating some metals from their solutions in the metallic state. If a of phosphorus be placed in a solution of sulphate of copper, it nes coated with metallic copper, the phosphorus appropriating the en. This has been turned to advantage in copying very delicate ts by the electrotype process, for by exposing them to the action of a on of phosphorus in ether or bisulphide of carbon, and afterwards to of a solution of copper, they acquire the requisite conducting metallic even on their finest filaments. Solutions of silver and gold are ed in a similar manner by phosphorus.

floating very minute scales of ordinary phosphorus upon a dilute solution of te of gold, the metal will be reduced in the form of an extremely thin film, may be raised upon a glass plate, and will be found to have various shades en and violet by transmitted light, dependent upon its thickness, whilst its st part exhibits the ordinary colour of the metal to reflected light. By heat- e films on the plate, various shades of amethyst and ruby are developed. If dilute solution of chloride of gold in distilled water be placed in a perfectly clean and a few drops of ether, in which phosphorus has been dissolved, poured , a beautiful ruby-coloured liquid is obtained, the colour of which is due to ic gold in an extremely finely divided state, and on allowing it to stand for months, the metal subsides as a purple powder, leaving the liquid colourless. saline impurity be present in the gold solution, the colour of the reduced gold e amethyst or blue. These experiments (Faraday) illustrate very strikingly se of gold for imparting ruby and purple tints to glass and the glaze of ain.

162. *Lucifer matches* are made by tipping the wood with sulphur ... wax or paraffine to convey the flame, and afterwards with the match ... position, which is generally composed of saltpetre or chlorate of pot... phosphorus, red lead, and glue, and depends for its action on the ... inflammation, by friction, of phosphorus when mixed with oxidising ... like saltpetre ($KO.NO_5$), chlorate of potash ($KO.ClO_5$), or red ... (Pb_3O_4), the glue only serving to bind the composition together ... attach it to the wood. The composition used by different makers ... much in the nature and proportions of the ingredients. In this co... chlorate of potash is most commonly employed as the oxidising ... such matches usually kindling with a slight detonation; but the G... manufacturers prefer either nitrate of potash or nitrate of lead, to... with binoxide of lead or with red lead, which produce *silent matches*.

Sulphide of antimony (which is inflamed by friction with chlor... potash, see p. 157) is also used in those compositions in which a p... the phosphorus is employed in the amorphous form, and fine ... powdered glass is very commonly added to increase the susceptib... of the mixture to inflammation by friction.

The match composition is coloured either with ultramarine blue, P... sian blue, or vermilion. In preparing the composition, the glue and ... nitre or chlorate of potash are dissolved in hot water, the phosphorus ... added and carefully stirred in until intimately mixed, the whole be... kept at a temperature of about 90° F. The fine sand and colou... matter are then added, and when the mixture is complete, it is spread ... upon a stone slab heated by steam, and the sulphured ends of the ma... are dipped into it.

The *safety matches*, which refuse to ignite unless rubbed upon the b... tom of the box, are tipped with a mixture of sulphide of antimo... chlorate of potash, and powdered glass, which is not sufficiently sensitive ... to be ignited by any ordinary friction, but inflames at once when rubbed ... upon the amorphous phosphorus mixed with glass which coats the rubber ... beneath the box. On this principle some French matches have been mad... which can be ignited only by breaking the match and rubbing the two ... ends together.

It would be very desirable to dispense entirely with the use of phos... phorus in lucifer matches, not only because of the danger from accident ... and disease in the manufacture, but because a very large quantity of ... phosphate of lime which ought to be employed for agricultural purposes ... is now devoted to the preparation of phosphorus, of which six tons are ... said to be consumed annually in this country for the manufacture of ... matches. The most successful attempt in this direction appears to be the ... employment of a mixture of chlorate of potash and hyposulphite of lead, ... in place of the ordinary phosphorus composition.

For illustration, very excellent matches may be made upon the small scale in the following manner. The slips of wood are dipped in melted sulphur so as to acquire a slight coating. 30 grains of gelatine or isinglass are dissolved in 2 drachms of water in a porcelain dish placed upon a steam-bath; 20 grains of ordinary phosphorus are then added, and well mixed in with a piece of stick; to this mixture are added, in succession, 15 grains of red lead and 50 grains of powdered chlorate of potash. The sulphured matches are dipped into this paste, and left to dry in the air.

To make the safety matches: 10 grains of powdered chlorate of potash and 10 grains of sulphide of antimony are made into a paste with a few drops of a warm solution of 20 grains gelatine in 2 drachms water, the sulphured matches being tipped with this composition. The rubber is prepared with 20 grains of amorphous

phosphorus, and 10 grains of finely-powdered glass, mixed with the solution of gelatine, and painted on paper or card-board with a brush.

163. *Phosphorus-fuze composition.*—To ignite the Armstrong percussion shells, a very sensitive detonating composition is employed, which is composed of amorphous phosphorus, chlorate of potash, shellac, and powdered glass made into a paste with spirit of wine. This is placed in the little cap designed for it, and when dry is waterproofed with a little shellac dissolved in spirit.

Such a composition may be prepared *with care* in the following manner:—4 grains of powdered chlorate of potash are moistened on a plate with 6 drops of spirit of wine, 4 grains of powdered amorphous phosphorus are added, and the whole mixed at arm's-length with a bone knife, avoiding great pressure. The mixture, which should still be quite moist, is spread in small portions upon ten or twelve pieces of filtering paper, and left in a safe place to dry. If one of these be gently pressed with a stick, it explodes with great violence. It is dangerous to press it with the blade of a knife, as the latter is commonly broken, and the pieces projected with considerable force. A stick dipped in oil of vitriol of course explodes it immediately. If a bullet be placed very lightly upon one of the pellets, and the paper tenderly wrapped round it, a percussion shell may be extemporised, which explodes with a loud report when dropped upon the floor.

Oxides of Phosphorus.

164. There are only two compounds of phosphorus with oxygen which have been obtained and satisfactorily examined in the separate state, viz., *phosphorous acid* (PO_3), and *phosphoric acid* (PO_5). The *sub-oxide of phosphorus* (P_2O) is said to have been obtained, but very little is known of it, and *hypophosphorous acid* (PO) has only been obtained in combination with water.

Oxides of Phosphorus.

Name.	Equivalent Formula.	By Weight.	
		Phosphorus.	Oxygen.
Suboxide of phosphorus?	P_2O	62	8
Hypophosphorous acid?	PO	31	8
Phosphorous acid	PO_3	31	24
Phosphoric acid	PO_5	31	40

Phosphoric Acid.

165. Phosphoric acid is by far the most important of the compounds of phosphorus. It has been already noticed as almost the only form of combination in which that element is met with in nature, and as an indispensable ingredient in the food of plants and animals. No other mineral substance can bear comparison with it as a measure of the capability of a country to support animal life. The acid itself is very useful in calico-printing and some other arts.

The mineral sources of this acid appear to be *phosphorite*, *coprolite*, and *apatite*, all consisting essentially of phosphate of lime ($3CaO . PO_5$), but associated in each case with fluoride of calcium, which is also contained, with phosphate of lime, in bones, and would appear to indicate an organic *origin for these minerals.* *Phosphorite* is an earthy-looking substa

forming large deposits in Estremadura. Apatite (from ἀπατάω, *to cheat*, in allusion to mistakes in its early analysis) occurs in prismatic crystals, and is met with in the Cornish tin-veins. Both these minerals are largely imported from Spain, Norway, and America, for use in this country as a manure.

Coprolites (κόπρος, *dung*, λίθος, *a stone*, from the idea that they were petrified dung) are rounded nodules of phosphate of lime, which are found abundantly in this country.

Large quantities of phosphoric acid, combined with lime and magnesia, are imported in the form of *guano*, the partially decomposed excrement of sea-fowl, which sometimes contains one-fourth of its weight of phosphoric acid.

Bones, however, must be regarded as the chief immediate source whence the phosphate of lime for agricultural purposes is derived.

Hydrated phosphoric acid is obtained from bone-ash by decomposing it with sulphuric acid, so as to remove as much of the lime as possible in the form of sulphate, which is strained off, and the acid liquid neutralised with carbonate of ammonia, which precipitates any unchanged phosphate of lime, and converts the phosphoric acid into phosphate of ammonia, consisting of phosphoric acid, water, and ammonia. On evaporating the solution, and heating the phosphate of ammonia, the ammonia is expelled, and hydrated phosphoric acid ($HO . PO_5$) is left in a fused state, solidifying to a glass on cooling. Thus prepared, however, it always retains some ammonia, and is contaminated with soda derived from the bones.

The pure hydrated acid is prepared by oxidising phosphorus with diluted nitric acid (sp. gr. 1·2), and evaporating the solution in a platinum dish, until the hydrated phosphoric acid begins to volatilise in white fumes—

$$5(HO . NO_5) + P_3 = 3(HO . PO_5) + 2HO + 5NO_2.$$

Fig. 205.

Some phosphorous acid is formed at an intermediate stage. A transparent glass (*glacial phosphoric acid*) is thus obtained, which eagerly absorbs *moisture* from the air, and becomes liquid.

er cannot be separated from the hydrated phosphoric acid by of heat, so that the *anhydrous phosphoric acid* must be pre- urning phosphorus in dry air.

uired in considerable quantity, the anhydrous phosphoric acid (*phos- ride*) is prepared by burning the phosphorus in a small porcelain dish attached to a wide glass tube (B) for introducing the phosphorus, and a glass flask with two lateral necks, one of which is connected with a ing pumice-stone and oil of vitriol for drying the air as it enters, whilst ck is provided with a wide tube conveying the anhydrous phosphoric ottle connected, at C, with an aspirator, or cistern of water, for drawing the apparatus. The first piece of phosphorus is kindled by passing a vn the wide tube, but afterwards the heat of the dish will always ignite ce as it is dropped in. The wide tube must be closed with a cork whilst rus is burning.

quantity of anhydrous phos- is more conveniently prepared phosphorus under a large bell- nder which a shallow dish of has been standing for an hour y the air. This dish is care- d without disturbing the air jar, and the well-dried phos- troduced in a small porcelain ding upon a large glass plate. orus having been kindled with the flakes of phosphoric acid falling like snow on to the glass they accumulate in a layer of thickness. To preserve it, ric acid must be immediately scraped up with a bone or platinum knife into a thoroughly dry stoppered bottle.

Fig. 206.

ous phosphoric acid may be fused at a very high temperature, sublimed. Its great feature is its attraction for water; left the air for a very short time, it deliquesces entirely, becoming into hydrated phosphoric acid. It is often used by chemists as *ing agent*, and will even remove the water from oil of vitriol. wn into water, it hisses like a red-hot iron, but does not entirely once, a few flakes of hydrated phosphoric acid remaining in the liquid for some time. Phosphoric acid, like sulphuric three definite combinations with water, but in the case of acid, each of these three hydrates is a different acid, capable ng different salts, whereas the sulphuric acid generates the same atever degree of hydration it is employed.

ution obtained by dissolving anhydrous phosphoric acid in tains *monohydrated phosphoric acid* or *metaphosphoric acid* . If a little nitrate of silver be added to a portion of it, a t gelatinous precipitate is formed, which is the metaphosphate $AgO.NO_5 + HO.PO_5 = HO.NO_5 + AgO.PO_5$).

olution of metaphosphoric acid be heated in a flask for a short ll lose the property of yielding a precipitate with nitrate of ss one or two drops of ammonia be added to neutralise it, when white precipitate of pyrophosphate of silver ($2AgO.PO_5$) is for the phosphoric acid has now been converted into the or *pyrophosphoric acid* ($2HO.PO_5$). The formation of the is thus expressed—

$$+ 2(AgO.NO_5) + 2NH_3 = 2AgO.PO_5 + 2(NH_3.HO.NO_5).$$

When the solution of pyrophosphoric acid is mixed with more wa and boiled for a long time, it gives, when tested with nitrate of sil and a little ammonia, a yellow precipitate of triphosphate of sil ($3AgO.PO_5$); the phosphoric acid having become converted into th *hydrated* phosphoric acid ($3HO.PO_5$), and acting upon the nitrate of sil in the presence of ammonia, thus—

$$3HO.PO_5 + 3(AgO.NO_5) + 3NH = 3AgO.PO_5 + 3(NH_3.HO.NO_5)$$

The *pyrophosphoric acid* ($2HO.PO_5$) cannot be obtained by the ab process without an admixture of one of the other hydrates, but it h been obtained in crystals by decomposing the pyrophosphate of l ($2PbO.PO_5$) with hydrosulphuric acid, and evaporating the filte solution *in vacuo* over oil of vitriol.

Trihydrated phosphoric acid may also be obtained in prismatic crysta by evaporating its solution in a similar way. This acid is also call *ortho-phosphoric acid* (ὀρθός, *true*), and *common* phosphoric acid, in allu to the circumstance that the phosphates commonly met with and employe in the arts are the salts of this acid.

For it will be perceived that each of these acids is able to combine wi a quantity of base equivalent to the water present in the hydrate. Th the metaphosphoric acid ($HO.PO_5$) is *monobasic*, or forms salts with on equivalent of a base having the general formula MO, as in metaphosphat of soda, $NaO.PO_5$. Pyrophosphoric acid ($2HO.PO_5$) is *dibasic* (o *bibasic*), forming salts with two equivalents of a basic protoxide, as in pyrophosphate of soda, $2NaO.PO_5$. Common phosphoric acid ($3HO.PO_5$) is *tribasic*, forming salts with three equivalents of a basic protoxide, as in triphosphate (or subphosphate) of soda, $3NaO.PO_5$.

In the cases of pyrophosphoric and common phosphoric acids, it is not necessary that the two or three equivalents of water should be displaced by the same base, for it is found that salts of these acids may be formed which contain two bases, and some in which part of the water does duty as a base. Examples of this kind are, the common phosphate of soda, $2NaO.HO.PO_5$, which is derived from the tribasic acid, $3HO.PO_5$, by the displacement of two equivalents of water by soda; *microcosmic salt*, or phosphate of soda and ammonia, $NaO.NH_4O.HO.PO_5$, where two equivalents of the water in the tribasic acid are displaced respectively by soda and by the imaginary oxide of ammonium (NH_4O). A pyrophosphate of soda having the composition $NaO.HO.PO_5$ may be prepared, and is obviously derived from the dibasic acid, $2HO.PO_5$, by the displacement of one equivalent of water by soda.

Fig. 207.

It is evident that when water or ammonia enters into the composition of the salt, the action of heat may convert a tribasic phosphate into a pyrophosphate, or even into a metaphosphate.

Thus, if a crystal of the common rhombic phosphate of soda ($2NaO.HO.PO_5 + 24Aq.$) be heated gently in a crucible (fig. 207), it melts in its water of crystallisation, and gradually dries up to a white mass, the composition of h, if not heated beyond 300° F., will be $2NaO.HO.PO_5$. If a little of this e mass be dissolved in water, the solution will be *alkaline* to red litmus paper; if nitrate of silver (itself neutral to test-papers) be added to it, a yellow

precipitate of triphosphate of silver will be obtained, and the solution will become strongly *acid*—

$$2(NaO.HO.PO_5) + 3(AgO.NO_5) = 3AgO.PO_5 + 2(NaO.NO_5) + HO.NO_5.$$

If the dried phosphate of soda be now strongly heated over a lamp, it will lose its basic water, and become pyrophosphate of soda (πῦρ, *fire*). On dissolving this in water, the solution will be *alkaline*, and will give with nitrate of silver a *white* precipitate and a *neutral* solution—

$$2NaO.PO_5 + 2(AgO.NO_5) = 2AgO.PO_5 + 2(NaO.NO_5).$$

Microcosmic salt ($NaO.NH_4O.HO.PO_5 + 8Aq$), when dissolved in water, yields an *alkaline* solution which gives a *yellow* precipitate with nitrate of silver, the liquid becoming *acid*—

$$NaO.NH_4O.HO.PO_5 + 3(AgO.NO_5) = 3AgO.PO_5 + NaO.NO_5 + NH_4O.NO_5 + HO.NO_5$$

But if the salt be heated in a crucible, it fuses, evolving water and ammonia, and leaving a transparent glass of metaphosphate of soda ($NaO.PO_5$), which may be dissolved by soaking in water, yielding a slightly *acid* solution, which gives a *white* gelatinous precipitate with nitrate of silver, the liquid being *neutral*—

$$NaO.PO_5 + AgO.NO_5 = AgO.PO_5 + NaO.NO_5.$$

The crystallised metaphosphate of soda retains 1 eq. of water when dried at 212° F., becoming $NaO.PO_5 + HO$. On heating this to 300° F., the salt is converted into the acid pyrophosphate of soda, $NaO.HO.PO_5$, the water having assumed a basic character in the salt.

All the phosphates may be converted into tribasic phosphates, by fusing them with an alkaline hydrate or carbonate.*

Composition of phosphoric acid.—When anhydrous phosphoric acid is dissolved in water, forming metaphosphoric acid, a quantity of the solution containing 71 parts by weight of the anhydrous acid is required to neutralise 1 eq. (31 parts) of soda (NaO), forming metaphosphate of soda. 71 parts of phosphoric acid have been found to be produced by burning 31 parts of pure phosphorus in dry air; hence (71 *minus* 31) 40 parts of oxygen or 5 eqs. are combined with 31 parts of phosphorus to form 71 parts (1 eq.) of phosphoric acid.

166. *Phosphorous acid* (PO_3) is the product of the slow combustion of phosphorus. If a piece of phosphorus be heated in a long glass tube, into which a very slow current of dry air is drawn through a very narrow tube, it burns with a pale blue flame, and white flakes of anhydrous phosphorous acid are deposited. Phosphorous acid is more easily converted into vapour than phosphoric acid. It eagerly absorbs moisture from the air, and is decomposed when strongly heated in a sealed tube, yielding free phosphorus and phosphoric acid; $5PO_3 = 3PO_5 + P_2$.

Hydrated phosphorous acid is obtained in solution, mixed with phosphoric acid, when sticks of phosphorus arranged in separate tubes, open at both ends, and placed in a funnel over a bottle, are exposed under a bell-jar, open at the top, to air saturated with aqueous vapour. To obtain the pure acid, chlorine is very slowly passed through phosphorus fused under water, when the terchloride of phosphorus first formed is decomposed by the water into phosphorous and hydrochloric acids; $PCl_3 + 6HO = 3HO.PO_3 + 3HCl$. The hydrochloric acid is expelled by a moderate heat, when the hydrated phosphorous acid is deposited in prismatic crystals. The water cannot be separated from phosphorous acid by heat; when the hydrate is heated, it is decomposed into hydrated phosphoric acid and gaseous phosphuretted hydrogen; $4(3HO.PO_3) = 3(3HO.PO_5) + PH_3$.

Solution of phosphorous acid gradually absorbs oxygen from the air, becoming phosphoric acid. This tendency to absorb oxygen causes it to act as a reducing agent upon many solutions; thus it precipitates finely-divided metallic silver from

* It has been remarked that the *pliancy* of the acid character of phosphoric acid particularly fits it to take part in the vital phenomena. It may be regarded as three acids *in one*.

a solution of the nitrate, by which its presence may be recognised in the water in which ordinary phosphorus has been kept. The solution of phosphorous acid even reduces sulphurous acid, producing sulphuretted hydrogen and sulphur, the latter being formed by the action of the sulphuretted hydrogen upon the sulphurous acid; $2SO_2 + 2HO + 8(3HO . PO_3) = 2HS + 8(3HO . PO_5)$.

Phosphorous acid was formerly supposed to be a tribasic acid like common phosphoric acid, but it has not been found possible to combine it with more than two equivalents of a basic protoxide. Thus, when solution of phosphorous acid is mixed with a slight excess of solution of soda, and carefully evaporated, crystals are deposited which have the composition $2NaO . PO_3 + 11HO$. From these crystals, however, only 10 eqs. of water can be separated, even at 570° F., leading to the belief that the elements of the last equivalent of water really belong to the acid itself, and that the true formula of the phosphite of soda dried at that temperature is $2NaO . HO . PO_3$, or $2NaO . PHO_4$. In support of this view, it is to be desired that the compound PHO_4 or $HO . PO_3$ should be obtained in a separate state. Granting that phosphorous acid is dibasic, it should form, like dibasic phosphoric acid, two classes of salts; accordingly, we find the acid phosphites containing only one equivalent of base, the absent equivalent being represented by water. Thus, acid phosphite of baryta dried at 212° F. has the composition $BaO . 2HO . PO_3$, or (allowing the existence of PHO_4) $BaO . HO . PHO_4$. When heated, the phosphites are converted into phosphates at the expense of the oxygen of the water contained in them, the hydrogen being evolved, often accompanied by phosphuretted hydrogen.

167. *Hypophosphorous acid.*—The anhydrous hypophosphorous acid is at present entirely imaginary. When phosphorus is boiled with hydrate of baryta and water, the latter is decomposed, its hydrogen combining with part of the phosphorus to form phosphuretted hydrogen (spontaneously inflammable), which escapes, whilst the oxygen of the water unites with another part of the phosphorus, forming hypophosphorous acid, which combines with baryta and water to form hypophosphite of baryta; this may be obtained by evaporating the solution, in crystals having the composition $BaO . 2HO . PO$. The action of phosphorus upon hydrate of baryta may be represented by the equation—

$$\underset{\text{Hydrate of baryta.}}{8(BaO . HO)} + 6HO + P_4 = \underset{\text{Hypophosphite of baryta.}}{8(BaO . 2HO . PO)} + \underset{\text{Phosphuretted hydrogen.}}{PH_3}.$$

Some phosphate of baryta ($3BaO . PO_5$) is also formed at the same time, as the result of a secondary action.

By dissolving the hypophosphite of baryta in water, and decomposing it with the requisite quantity of sulphuric acid, so as to precipitate the baryta as sulphate, a solution is obtained which may be concentrated by careful evaporation till it has the composition represented by the formula $3HO . PO$. If this hydrated hypophosphorous acid be heated, it evolves phosphuretted hydrogen, and becomes converted into hydrated phosphoric acid; $2(3HO . PO) = 3HO . PO_5 + PH_3$. When exposed to the air it absorbs oxygen, and becomes converted into phosphorous and phosphoric acids. It is a more powerful reducing agent than phosphorous acid. The latter acid does not reduce a solution of sulphate of copper, but hypophosphorous acid, when gently warmed with it, gives a black precipitate of *subhydride of copper* (Cu_2H), which is decomposed by boiling, evolving hydrogen and leaving metallic copper.

The composition of the hydrated hypophosphorous acid ($3HO . PO$) formerly led to the belief that this acid was tribasic, but it is found incapable of generating salts which contain more than 1 eq. of basic protoxide. These always retain the elements of 2 eqs. of water, even though exposed to a high temperature. Thus the dried hypophosphite of baryta contains $BaO . 2HO . PO$. Hence it is often represented as $BaO . PH_2O_3$, when the hydrated acid would be $HO . PH_2O_3$ ($= 3HO . PO$), and would be a monobasic acid like metaphosphoric acid. When heated, the hypophosphites evolve phosphuretted hydrogen, and are converted into phosphates. The hypophosphite of soda ($NaO . PH_2O_3$) is sometimes used in medicine; its solution has been known to explode with great violence during evaporation, probably from a sudden engagement of phosphuretted hydrogen.

It will be noticed that the phosphites may be represented as pyrophosphates, in which 1 eq. of oxygen in the phosphoric acid has been displaced by hydrogen. Thus, pyrophosphate of soda ($2NaO . PO_5$) one equivalent of oxygen in the acid be displaced by hydrogen, it would give phosphite of soda ($2NaO . PHO_4$), and in a similar

nner, hypophosphite of soda ($NaO.PH_2O_3$) may be represented as derived from taphosphate of soda ($NaO.PO_4$) by the displacement of two equivalents of oxygen the acid by hydrogen.

168. *Suboxide of phosphorus* is supposed to constitute the yellow or red residue ich is left in the dish when phosphorus rns in air, but it is always mixed with much osphoric acid. If phosphorus be melted der water in a flask (fig. 208), and oxygen s be allowed to bubble through it (a brass be being employed to convey the oxygen), ch bubble of the gas produces a brilliant sh, and the phosphorus is converted into d flakes, which were believed to be suboxide phosphorus, but are probably amorphous osphorus. The true suboxide of phosphorus P_2O) appears to be formed when small pieces phosphorus are covered with terchloride of hosphorus, exposed to the air, and afterwards eated with water, when the suboxide is deposited as a yellow powder, becoming ed at high temperatures, and inflaming when heated in air.

Fig. 208.

Phosphides of Hydrogen.

169. Although phosphorus and hydrogen do not combine directly, there are three compounds of these elements producible by processes of substitution, the composition of which is shown in the following table :—

Name.	Equivalent Formula.	By Weight.	
		Phosphorus.	Hydrogen.
Phosphuretted hydrogen gas . . .	PH_3	31	3
Liquid phosphide of hydrogen . .	PH_2	31	2
Solid phosphide	P_2H ?	62	1

Phosphuretted hydrogen gas is by far the most important of these. It as been mentioned above as resulting from the action of heat upon ydrated phosphorous acid, and when repared by this process it is obtained as a colourless gas, with a ost powerful odour of putrid fish, nflaming on the approach of a light, nd burning with a brilliant white ame, producing thick clouds of hosphoric acid. It is slightly eavier than air (sp. gr. 1·19), and as been liquefied under high pressure.

Fig. 209.—Preparation [illegible] etted hydro[illegible]

The ordinary method of preparing this as for experimental purposes consists in oiling phosphorus with a strong solution f potash, when water is decomposed, its ydrogen combining with one part of the hosphorus, *and its oxygen with another forming hypop[illegible] which nites with the potash.*

A few fragments of phosphorus are introduced into a small retort (fig. 209), which is then nearly filled with a strong solution of potash (sp. gr. 1·3*), and heated. The extremity of the neck of the retort should not be plunged under water until the spontaneously inflammable gas is seen burning at the orifice, and the retort must not be placed close to the face of the operator, since explosions sometimes take place in preparing the gas, and the boiling potash produces dangerous effects. The gas may be collected in small jars filled with water, taking care that no bubble of air is left in them. It contains phosphuretted hydrogen, mixed with free hydrogen, the latter being formed from the deoxidation of water by the hypophosphite of potash. As each bubble of this gas escapes into the air through the water of the pneumatic trough, it burns with a vivid white flame, producing beautiful wreaths of smoke (phosphoric acid), resembling *gunner's rings* sometimes seen in firing cannon. Small bubbles sometimes escape without spontaneously inflaming. If a bubble be sent up into a jar of oxygen, the flash of light is extremely vivid, and the jar must be a strong one to resist the concussion. It is advisable to add a trace of chlorine to the oxygen to insure the inflammation of each bubble, for an accumulation of the gas would shatter the jar.

If this gas be passed through a tube cooled in a freezing mixture of ice and salt, the gas escaping from the tube is found to have lost its spontaneous inflammability, although it takes fire on contact with flame. The cold tube contains the *liquid phosphide of hydrogen* (PH_2), which was present in the gas in the state of vapour, and caused its spontaneous inflammability, for as soon as this liquid comes in contact with air it takes fire. When exposed to light, the liquid phosphide is decomposed into phosphuretted hydrogen gas and a yellow *solid phosphide* (P_2H), which is not spontaneously inflammable; $5PH_2 = P_2H + 3PH_3$. It is for this reason that the spontaneously inflammable gas loses that property when kept (unless in the dark), depositing the solid phosphide upon the sides of the jar.

By passing a few drops of oil of turpentine up through the water into a jar of the spontaneously inflammable gas, this property will be entirely destroyed, whereas the addition of a trace of nitrous acid imparts spontaneous inflammability.

Phosphuretted hydrogen, when passed through solutions of some of the metals, precipitates their phosphides. For example, with sulphate of copper it gives a black precipitate of phosphide of copper—

$$3(CuO.SO_3) + PH_3 = 3(HO.SO_3) + PCu_3 .$$

When this black precipitate is heated with solution of cyanide of potassium, it evolves self-lighting phosphuretted hydrogen.† In fact this is one of the easiest and safest methods of preparing this gas; for the phosphide of copper is readily obtained by simply boiling phosphorus in a solution of sulphate of copper.

Phosphuretted hydrogen has great pretensions to rank as the chemical analogue of ammonia, for although it has no alkaline properties, it is capable of combining with hydrobromic and hydriodic acids to form crystalline compounds analogous to the hydrobromate and hydriodate of ammonia; these compounds, however, are decomposed by water. It will be seen hereafter, that when the hydrogen of phosphuretted hydrogen is displaced by certain compound radicals, such as ethyle, powerful organic bases are produced.

The spontaneously inflammable phosphuretted hydrogen may also be obtained by throwing fragments of *phosphide of calcium* into water; this substance is prepared by passing vapour of phosphorus over red-hot quick-lime, or simply by heating small lumps of quick-lime to redness in a crucible and throwing in fragments of phosphorus, closing the crucible immediately. The dark brown mass thus obtained is a mixture of pyrophosphate of lime and phosphide of calcium of somewhat variable composition.

170. *Composition of phosphuretted hydrogen gas.*—Analysis has shown this gas to contain 31 parts by weight of phosphorus combined with 3 parts by weight of hydrogen, or 1 eq. of phosphorus and 3 eqs. of hydrogen. It combines with an equal volume of hydriodic acid gas, and the compound is found to contain 34 parts by weight of phosphuretted hydro-

*50 grains of common stick potash dissolved in 1000 grains of water.

†Cyanide of copper and phosphide of potassium being formed, and the latter decomposed by water, giving phosphuretted hydrogen, and hypophosphite of potash.

, and 128 parts (1 eq.) of hydriodic acid. But 1 eq. of hydriodic acid
upies 4 vols. (O = 1 vol.), therefore 1 eq. of phosphuretted hydrogen
upies 4 vols. The specific gravity of the gas (or weight of 1 vol.)
ng 1·185, the weight of 4 vols. will be 4·740. But 3 eqs. of hydrogen
upy 6 vols.

4 vols. PH_3 weigh, ...	4·740
6 vols. H (.069 × 6)	·414
Weight of phosphorus vapour, . . .	4·326

ıtained in 4 vols. PH_3. The specific gravity of phosphorus vapour is
0, so that, allowing for errors of experiment, the above number repre-
ıts 1 vol. of the vapour.

1 eq. or 4 vols. of PH_3, therefore, contain 1 eq. or 1 vol. of phosphorus
pour, and 3 eqs. or 6 vols. of hydrogen. Unfortunately this is not
alogous to the composition of ammonia (NH_3), in which the 1 eq. of
trogen occupies 2 vols. The *molecular formula* of phosphuretted
drogen, on the assumption that 1 vol. of vapour of phosphorus repre-
nts one atom, would, of course, be PH_6, but the chemical resemblance
tween that substance and ammonia is so great,* that preference is given
the molecular formula PH_3 (= 2 vols.), when P represents only $\frac{1}{2}$ vol.
vapour (H = 1 vol.), it being hoped that future investigation may re-
ove the anomaly. When phosphuretted hydrogen is decomposed by a
ıccession of electric sparks, 2 vols. of the gas yield 3 vols. of hydrogen,
d phosphorus being deposited. Assuming 31 to represent the atomic
eight of phosphorus, the atomic formula of anhydrous phosphoric acid
ould be P_2O_5 (O = 16), and that of the trihydrated or common phos-
horic acid H_3PO_4.

171. The *chlorides of phosphorus* correspond in composition to phosphorous and
osphoric acids. The *terchloride* (PCl_3) is prepared by acting upon phosphorus
th perfectly dry chlorine in the apparatus employed (p. 219) for preparing the
hloride of sulphur. Terchloride of phosphorus distils over very easily (boiling
int, 173°·4 F.), as a colourless pungent liquid (sp. gr. 1·62), which fumes strongly
air, its vapour decomposing the moisture of the air and producing hydrochloric
d fumes. In contact with water the liquid is immediately decomposed, yielding
drochloric and phosphorous acids, as described for the preparation of the latter
d (p. 233). Its analogy to anhydrous phosphorous acid is shown by its absorb-
oxygen when boiled in the presence of that gas, and forming the *oxychloride of*
sphorus (PCl_3O_2), corresponding in composition to anhydrous phosphoric acid. It
o absorbs chlorine with avidity, becoming converted into *pentachloride of phosphorus*
(PCl_5). This compound, however, is more conveniently prepared by passing
lorine through a solution of phosphorus in bisulphide of carbon, carefully cooled.
evaporation, the pentachloride of phosphorus is deposited in white prismatic
rstals, which volatilise below 212° F., and fume when exposed to air, from the pro-
ction of hydrochloric acid. When thrown into water it is decomposed into phos-
oric and hydrochloric acids; $PCl_5 + 8HO = 3HO.PO_5 + 5HCl$. But if it be
owed to deliquesce in air, only a partial decomposition takes place, and the
ychloride of phosphorus is formed; $PCl_5 + 2HO = PCl_3O_2 + 2HCl$.
This oxychloride of phosphorus may also be produced by heating pentachloride
phosphorus with anhydrous phosphoric acid; $2PO_5 + 3PCl_5 = 5PCl_3O_2$. A
re instructive method of preparing it consists in distilling the pentachloride of
osphorus with crystallised boracic acid—

$$3PCl_5 + 2(3HO.BO_3) = 3PCl_3O_2 + 6HCl + 2BO_3.$$

Some of the hydrated organic acids (succinic, for example) may be obtained in

* Moreover, the specific heat of phosphorus agrees much more closely with an atomic
ight of 31 (= ½ vol.) than with 62 (= 1 vol.)

the anhydrous state, as the boracic acid is in this case, by distillation with pen... chloride of phosphorus. The oxychloride of phosphorus distils over (boiling-po... 230° F.) as a heavy (sp. gr. 1·7) colourless fuming liquid of pungent odour. ... course it is decomposed by water, yielding hydrochloric and phosphoric acids... will be found of the greatest use in effecting certain transformations in organic ... stances.

The analogy between water and hydrosulphuric acid would lead to the expe... tion that a *sulphochloride of phosphorus* (PCl_3S_2), corresponding to the oxychlo... would be formed by the action of hydrosulphuric acid upon pentachloride of ph... phorus; $PCl_5 + 2HS = PCl_3S_2 + 2HCl$. It is a colourless fuming liquid, wh... is slowly decomposed by water, giving phosphoric, hydrochloric, and hydrosulph... acids; $PCl_3S_2 + 8HO = 3HO.PO_5 + 3HCl + 2HS$. When acted on by a... tion of soda, the sulphochloride of phosphorus loses its chlorine to the sod... and acquires an equivalent quantity of oxygen, a *sulphoxy-phosphate of so...* ($3NaO.PO_3S_2 + 24HO$) being deposited in crystals. This salt evidently cor... sponds in composition to the triphosphate of soda ($3NaO.PO_5 + 24HO$), and its pr... duction is expressed by the equation; $PCl_3S_2 + 6NaO = 3NaCl + 3NaO.PO_3S_2$. Since salts of similar composition may be obtained with other metallic oxides, the... probably exists a sulphoxy-phosphoric acid (PO_3S_2) corresponding to phosphor... acid.

The terchloride of phosphorus (PCl_3) contains 1 vol. of phosphorus vapour an... 6 vols. of chlorine, condensed into the space of 4 vols. (O = 1 vol.), its vapour... density being 4·875.

The pentachloride (PCl_5) having a vapour density of 3·654, contains 1 vol. o... phosphorus vapour and 10 vols. of chlorine condensed into 8 vols. of pentachloride... of phosphorus vapour.*

In the oxychloride of phosphorus (PCl_3O_2), however, 1 vol. of phosphorus vapour, 6 vols. of chlorine, and 2 vols. of oxygen, are condensed into 4 vols., the specific... gravity of its vapour being 5·29.

The composition by volume of the sulphochloride (PCl_3S_2) corresponds to that of... the oxychloride, 2 vols. of sulphur vapour (at 1900° F.) occupying the place of the... 2 vols. of oxygen, so that the specific gravity of the vapour of sulphochloride of phos... phorus is 5·878.

The *bromides* and *oxybromide of phosphorus* correspond to the chlorine compounds.

Iodine in the solid state combines very energetically with phosphorus, but if the two elements be brought together in a state of solution in bisulphide of carbon, a more moderate action ensues, and two *iodides of phosphorus* may be obtained in crystals; a teriodide (PI_3) corresponding to the terchloride, and a biniodide (PI_2), which has no analogue either among the oxygen, chlorine, or bromine compounds of phosphorus.

The addition of a very small quantity of iodine to ordinary phosphorus, fused in a flask filled with carbonic acid gas, materially accelerates its conversion into the red modification, and allows the change to be effected at a much lower temperature than that required when the phosphorus is heated alone. This has been ascribed to the disposition of the electro-negative iodine to cause the phosphorus to assume the positive or amorphous state when entering into combination with it; this compound being decomposed by heat with separation of amorphous phosphorus, the iodine combines with a fresh portion of the phosphorus, which is converted in the same way.

172. The *sulphides of phosphorus* may be formed by the direct combination of their elements. If ordinary phosphorus be used, the experiment is not unattended with danger, and should be performed under water. It is safer to combine the amorphous phosphorus with sulphur, at a moderate heat, in an atmosphere of carbonic acid.

There appear to be at least three sulphides of phosphorus corresponding to the oxides, viz., the protosulphide (PS) corresponding to the imaginary anhydrous hypophosphorous acid (PO), the tersulphide (PS_3), representing phosphorous acid (PO_3), and the pentasulphide (PS_5), analogous to phosphoric acid (PO_5).

* This is an exception to the rule, that the equivalents of compound vapours usually ... by 4 vols. (O = 1 vol.) But it appears that, at the temperature (572° F.) at which ... pour density of pentachloride of phosphorus is determined, it undergoes dissocia... ...wing a mixture of 4 vols. of terchloride of phosphorus and 4 vols. of chlorine, the ... of which is visible in the tube in which the vapour is heated.

PS is a yellow oily liquid which may be distilled out of contact with air.

PS_2 is a yellow solid, easily fusible, and capable of subliming in a crystalline form if air be excluded. It may be produced by the action of hydrosulphuric acid upon terchloride of phosphorus; $PCl_3 + 3HS = PS_3 + 3HCl$.

PS_5 crystallises more readily in a fused state than PS_3. Both these sulphides, like the protosulphide, are easily decomposed by water. All the sulphides are sulphur-acids like their prototypes among the oxides of phosphorus.

173. *Action of ammonia upon anhydrous phosphoric acid.*—Some remarkably stable and definite compounds, containing nitrogen and phosphorus, are derived from the action of ammonia on anhydrous phosphoric acid, and the study of their mode of formation will be found to throw some light upon the history of a very large and important class of organic substances known as the *amides*. Anhydrous phosphoric acid absorbs ammoniacal gas with great evolution of heat, and produces, not phosphate of ammonia, for that cannot be formed unless water is present, but the ammoniacal salt of a new acid, *phosphamic acid*, which contains the elements of acid phosphate of ammonia ($NH_4O.2HO.PO_5$) *minus* four equivalents of water—

$$NH_3 + PO_5 = HO + \underset{\text{Phosphamic acid.}}{NH_2PO_4}.$$

When gently heated with water, phosphamic acid is converted into acid phosphate of ammonia.

When the phosphamate of ammonia is heated in a current of dry ammonia, it gives off water, and leaves a yellow insoluble substance formerly supposed to be *phosphide of nitrogen*, but now known as *phospham*—

$$\underset{\text{Phosphamate of ammonia.}}{NH_3.HO.NH_2PO_4} = 5HO + \underset{\text{Phospham.}}{N_2HP}.$$

It is not surprising that the presence of hydrogen in this substance should have been overlooked, for it may be heated to redness (out of contact with air) without alteration, is unaffected by chlorine, and is very slowly acted upon by nitric acid.

Action of ammonia on oxychloride of phosphorus.

$$\underset{\substack{\text{Oxychloride of}\\\text{phosphorus.}}}{PCl_3O_2} + 3NH_3 = 3HCl + \underset{\text{Phosphotriamide.}}{N_3H_6PO_2}.$$

Of course the hydrochloric acid combines with the excess of ammonia to form hydrochlorate of ammonia, which may be washed out with water, leaving the phosphotriamide as a white insoluble solid, not easily attacked by acids or alkalies. It may be regarded as triphosphate of ammonia ($3NH_4O.PO_5$) *minus* six equivalents of water.

If sulphochloride of phosphorus be submitted to the action of ammonia, sulphophotriamide is obtained—

$$\underset{\substack{\text{Sulphochloride of}\\\text{phosphorus.}}}{PCl_3S_2} + 3NH_3 = 3HCl + \underset{\text{Sulphosphotriamide.}}{N_3H_6PS_2}.$$

This compound may evidently be regarded as sulphophosphate of (sulphide of) ammonium ($3NH_4S.PS_5$) *minus* six equivalents of hydrosulphuric acid.

Action of ammonia on pentachloride of phosphorus.

$$PCl_5 + 2NH_3 = 2HCl + \underset{\text{Chlorophosphamide.}}{N_2H_4PCl_3}.$$

The hydrochloric acid combines with the excess of ammonia, forming hydrochlorate of ammonia. By boiling chlorophosphamide with water, a very stable insoluble substance is obtained, known as *phosphodiamide*—

$$\underset{\text{Chlorophosphamide.}}{N_2H_4PCl_3} + 2HO = \underset{\text{Phosphodiamide.}}{N_2H_3PO_2} + 3HCl.$$

This substance may be represented as derived from the phosphate of ammonia ($2NH_4O.HO.PO_5$), by the abstraction of six equivalents of water.

When phosphodiamide is heated it loses ammonia and becomes *monophosphamide*—

$$\underset{\text{Phosphodiamide.}}{N_2H_3PO_2} = NH_3 + \underset{\text{Monophosphamide.}}{NPO_2}.$$

which may be regarded as acid phosphate of ammonia ($NH_4O.2HO.PO_5$) minus six equivalents of water.

The phrase *amides of phosphoric acid* refers to those substances which may be represented as derived from the phosphates of ammonia by the loss of a certain number of equivalents of water; thus—

$NH_4O.2HO.PO_5$	— 6HO	=	NPO_2	Monophosphamide.
$2NH_4O.HO.PO_5$	— 6HO	=	$N_2H_2PO_2$	Phosphodiamide.
$3NH_4O.PO_5$	— 6HO	=	$N_3H_6PO_2$	Phosphotriamide.

All these substances yield ammonia and phosphate of potash when heated with hydrate of potash, when they acquire the elements of water.

ARSENIC.

174. This element is often classed among the metals, because it has a metallic lustre and conducts electricity, but it is not capable of forming a base with oxygen, and the chemical character and composition of its compounds connect it in the closest manner with phosphorus.

In its mode of occurrence in nature it more nearly resembles the sulphur group of elements, for it is occasionally found in the uncombined state (*native arsenic*), but far more abundantly in combination with various metals, forming *arsenides*, which frequently accompany the sulphides of the same metals. The following are some of the chief arsenides and *arsenio-sulphides* found in the mineral kingdom:—

Kupfernickel,	Ni_2As.
Arsenical nickel,	$NiAs$.
Tin-white cobalt,	$CoAs$.
Mispickel or arsenical pyrites,	$FeS_2.FeAs$.
Cobalt-glance,	$CoS_2.CoAs$.
Nickel-glance,	$NiS_2.NiAs$.

But arsenic also occurs, like the metals, in combination with sulphur, thus we have—

Red orpiment or realgar,	AsS_2.
Yellow orpiment,	AsS_3.

It is from these minerals that arsenic derives its name (ἀρσενικὸν, *orpiment*), and the sulphides of arsenic being sulphur-acids, are found in combination with other sulphides; thus, *red silver ore* is a compound of the sulphides of silver and arsenic ($3AgS.AsS_3$); *Tennantite* contains sulphide of arsenic combined with the sulphides of iron and copper; and *grey copper ore* is composed of sulphide of arsenic with the sulphides of copper, silver, zinc, iron, and antimony. In an oxidised form arsenic is found in *conderrite*, which contains arsenious acid (AsO_3) and suboxide of copper. *Cobalt-bloom* consists of arseniate of cobalt ($3CoO.AsO_5$).

Arsenical pyrites is one of the principal sources of arsenic and its compounds, though a considerable quantity is also obtained in the form of arsenious acid as a secondary product in the working of certain ores, especially those of copper, tin, cobalt, and nickel.

The substance used in the arts under the name of arsenic is really the oxide of arsenic or arsenious acid (AsO_3); pure arsenic itself has very few useful applications, so that it is not the subject of an extensive manufacture. It can be extracted from arsenical pyrites ($FeS_2.FeAs$) by heating it in earthen cylinders fitted with iron receivers, in which the arsenic condenses as a metallic-looking crust, the heat expelling it from the pyrites in the form of vapour.

n a small scale it may be obtained by heating a mixture of arsenious acid with
f its weight of recently calcined charcoal in a crucible (fig. 210), the mixture
ng covered with two or three inches of char-
l in very small fragments, and the crucible so
ced that this charcoal may be heated to red-
s first, in order to ensure the reduction of any
enious acid which might escape from below.
order to collect the arsenic, another crucible,
ving a small hole drilled through the bottom
the escape of gas, is cemented on to the first,
an inverted position, with fire-clay, and pro-
ted from the fire by an iron plate with a hole
it for the crucible. The reduction of arseni-
s acid by charcoal is thus represented—

Fig. 210.—Extraction of arsenic.

$$As_2O_3 + C_3 = As + 3CO .$$

For the sake of illustration, a small quantity
arsenic may be prepared from arsenious acid
a method commonly employed in testing for
at substance. A small tube of German glass
drawn out to a narrow point (A. fig. 211), and sealed with the aid of the blow-
pe. A very minute quantity of arsenious acid is introduced into the point of the
be, and a few fragments of
arcoal are placed in the tube
elf at B. The charcoal is
ated to redness with a blow-
pe flame, and the point is
en heated so as to drive the
senious acid in vapour over
e red-hot charcoal, when a
hining black ring of arsenic
0) will be deposited upon the
oler portion of the tube.

Fig. 211.—Reduction of arsenious acid.

The arsenic thus obtained
a brittle mass of a dark
teel-grey colour and bril-
iant metallic lustre (sp.
r. 5·7). It does not fuse when heated, unless in a sealed tube, since it
converted into vapour at 356° F. It is not changed by exposure to air,
nless powdered and moistened, when it is slowly converted into arsenious
id. When heated in air, it oxidises rapidly at about 160° F., giving off
hite fumes of arsenious acid and a characteristic garlic odour (recalling
at of phosphorus). At a red heat it burns in air with a bluish white
me, and in oxygen with great brilliancy. It is not dissolved by water
any simple solvent (herein resembling the metals), but is oxidised and
solved by nitric acid.

In its chemical relations to other elements, arsenic much resembles
osphorus, undergoing spontaneous combustion in chlorine, and easily
mbining with sulphur. Like phosphorus also, it combines with many
tals, even with platinum, to form arsenides, and its presence often
ects materially the properties of the useful metals. There are some
sons for believing in the existence of two allotropic forms of arsenic
fering in chemical activity like those of phosphorus.

Pure arsenic does not produce symptoms of poisoning till a considerable
riod after its administration, being probably first oxidised in the stomach
d intestines, and converted into arsenious acid.

Oxides of Arsenic.

175. Arsenic forms two well-defined acids with oxygen, correspondi to phosphorous and phosphoric acids.

	Equivalent Formula.	By Weight.	
		Arsenic.	Oxygen.
Arsenious acid,	AsO_3	75	24
Arsenic acid,	AsO_5	75	40

Arsenious acid.—Unlike phosphorus, arsenic, when burning in only combines with three equivalents of oxygen. Arsenious acid, *white arsenic*, is a very useful substance in many branches of indust It is employed in the manufacture of glass, of several colouring-matt and of shot. A large quantity is also consumed for the preparation arsenic acid and arseniate of soda; it is, indeed, the source from wh nearly all the compounds of arsenic are procured. Small quantities crystalline arsenious acid are occasionally found associated with the of nickel and cobalt.

Arsenious acid is manufactured by roasting the arsenical pyrites, chi obtained from the mines of Silesia, in *muffles* or ovens, through wh air is allowed to pass, when the arsenic is converted into arsenious a and the sulphur into sulphurous acid, which are conducted into l chambers, in which the arsenious acid is deposited as a very fine pow The iron of the pyrites is left partly as oxide, and partly as sulphat iron. The removal of the arsenious acid from the condensing chamb is a very unwholesome operation, owing to its dusty and very poison character. The workmen are cased in leather, and protect their mou and noses with damp cloths, so as to avoid inhaling the fine powder.

This rough arsenious acid is subjected to a second sublimation smaller scale in iron vessels, when it is obtained in the form of a s transparent glassy mass known as *vitreous arsenious acid*, which gradu becomes opaque when kept, and ultimately resembles porcelain. white arsenic sold in the shops is a fine powder, dangerously resemb flour in appearance, but so much heavier (sp. gr. 3·7) that it ought no be mistaken for it. When examined under the microscope, it appear the form of irregular glassy fragments, mixed with octahedral crys Arsenious acid softens when gently heated, but does not fuse (unless sealed tube), being converted into vapour at 380° F., and depositin brilliant octahedral crystals upon a cool surface. The experiment ma made in a small tube sealed at one end, the upper part of which sh be slightly warmed before heating the arsenious acid, so as to prevent rapid condensation, which is unfavourable to the formation of dist crystals.* The octahedra are best examined with a binocular microsc This common poison may fortunately be still more easily recognise sprinkling it upon a red-hot coal, when a strong odour of garlic is pe tible, due to the reduction of the acid by the heated carbon; the va of arsenious acid itself is inodorous. The sparing solubility of arsen

* When arsenious acid is fused in a long tube, sealed at both ends, and buried i sand, the mass, after cooling, is found to contain some prismatic crystals, which are *sublimed* on those parts of the tube which have been heated above 380° F.

d in water is very unfavourable to its action as a poison, for, when own into ordinary liquids, it is dissolved in very small quantity, the ater part of it collecting at the bottom. Even when arsenious acid is en into the stomach in a solid state, its want of solubility delays its ssage into the blood sufficiently to give a better chance of antidotal atment than in the case of most other common poisons. Its compara- e insolubility is shown by its being almost tasteless.

When thrown into water, arsenious acid exhibits great repulsion for e particles of that liquid, and collects in a characteristic manner round tle bubbles of air, forming small white globes which are not wetted by e water. Even if the acid be stirred with the water, and allowed to main in contact with it for some hours, a pint of water (20 oz.) would t take up more than 20 grs. of arsenious acid. The smallest dose which s been known to prove fatal is 2·5 grs. If boiling water be poured on powdered arsenious acid, and allowed to remain in contact with it ll cold, it will dissolve about $\frac{1}{110}$ of its weight (22 grs. in a pint).

When powdered arsenious acid is boiled with water for two or three ours, 100 parts by weight of water may be made to dissolve 11·5 parts f the acid, and when the solution is allowed to cool, about 9 parts of the id will be deposited in octahedral crystals, leaving 2·5 parts dissolved 100 of water (219 grs. in a pint).

This great increase in the solubility of the arsenious acid by long boiling ith water is usually attributed to the conversion of the opaque or crys- lline variety of the acid, which always composes the powder, into the itreous modification, which is the more soluble in water. Water, heated ith arsenious acid in a sealed tube, may be made to dissolve its own eight of the acid; as the solution cools, it first deposits prismatic crystals, nd afterwards the ordinary octahedral form. The solution of arsenious id is very feebly acid to blue litmus paper.

Arsenious acid dissolves abundantly in hot hydrochloric acid (a part of being converted into terchloride of arsenic), and as the solution cools, rt of the acid is deposited in large octahedral crystals. It is said that the vitreous acid be dissolved in hydrochloric acid, the formation of ese crystals will be attended by flashes of light, visible in a darkened om; but the opaque variety does not exhibit this phenomenon.

The vitreous arsenious acid has a slightly higher specific gravity than e opaque form, and fuses rather more easily. The opaque variety appears be identical in its properties with crystallised arsenious acid.

Solutions of the alkalies readily dissolve arsenious acid, forming alkaline enites, the solutions of which are capable of dissolving arsenious acid re easily than water, and deposit it in crystals on cooling. Arsenious d is sometimes deposited in *prismatic* crystals from its solution in tash, and the same form of crystallised arsenious acid has been found tive. On adding a small quantity of hydrochloric acid to the solution the alkaline arsenite, a white precipitate of arsenious acid is formed.

Arsenious acid has the property of preventing the putrefaction of skin d similar substances, and is occasionally employed for the preservation objects of natural history, &c.

Composition of arsenic acid and arsenious acid.—The chemical resem- ance between arsenic acid and phosphoric acid is so strong as to lead to e belief that they resemble each other in composition, and that, as osphoric acid is PO_5, *so arsenic acid* must be represented by AsO_5. *alyses have shown that in arsenic acid* the 5 equivalents (40 parts by

weight) of oxygen are combined with 75 parts by weight of arsenic, and this number may be assumed to represent the equivalent of arsenic. In arsenious acid it is found that 75 parts of arsenic are combined with 24 parts of oxygen, or 3 equivalents, and hence that acid may be represented by the formula AsO_3, rendering it the analogue of anhydrous phosphorous acid.

The specific gravity, or weight of 1 volume of AsO_3 vapour = 13·85
Deducting that of vapour of arsenic, = 10·60

3·25

the difference represents nearly the weight of 3 volumes (1·1057 × 3) of oxygen. Hence, 1 volume of arsenious acid vapour contains 1 volume of vapour of arsenic and 3 volumes of oxygen, and the equivalent volume of arsenic is 1, like that of phosphorus. The *molecular formula* of arsenious acid should be $(As\Theta_3)_2$, according to the experimental results stated above, representing 2 volumes of its vapour, the symbol As standing for 1 volume or 1 atom of arsenic (150 parts by weight), and Θ_3 for 3 volumes of oxygen (48 parts by weight); but since the specific heat of arsenic indicates 75 as its atomic weight, the molecular formula of arsenious acid is generally written $(As_2\Theta_3)_2$, 1 atom of arsenic vapour being taken to occupy ½ volume.

The atomic formula of arsenic acid would then be written $As_2\Theta_5$.

Arsenites.—Arsenious acid does not destroy the alkaline reaction of the alkalies, and it does not decompose the alkaline carbonates unless heat is applied, proving it to be a feeble acid. The arsenite of ammonia is very unstable, evolving ammonia freely when exposed to the air. When arsenious acid is dissolved in a hot solution of ammonia, octahedral crystals of the acid are deposited on cooling, notwithstanding the presence of ammonia in large excess.

When the carbonates of potash and soda are fused with an excess of arsenious acid, brilliant transparent glasses are obtained which are similar in composition to glass of borax ($KO.2AsO_3$ and $NaO.2AsO_3$).

If an alkaline arsenite be fused in contact with platinum, the latter is easily melted, combining with a small proportion of arsenic to form a fusible arsenide of platinum, a portion of the arsenious acid being converted into arsenic acid; $5AsO_3 = 3AsO_5 + As_2$. The alkaline arseniates are so much more stable than the arsenites, that the latter exhibit a great tendency to pass into the former, with separation of arsenic.

In consequence of the feeble acid character of arsenious acid, and the want of stability of the alkaline arsenites, there is some difficulty in ascertaining whether it is a monobasic acid or otherwise. The arsenite of silver ($3AgO.AsO_3$), however, contains 3 eqs. of oxide of silver (348 parts) combined with 1 eq. (99 parts) of arsenious acid; and arsenite of zinc ($3ZnO.AsO_3$) contains 3 eqs. of oxide of zinc (122·1 parts) combined with 1 eq. of arsenious acid. Moreover, the arsenite of magnesia, dried at 400° F., has the composition $2MgO.HO.AsO_2$, so that arsenious acid would appear to be a tribasic acid, though there are not wanting arsenites, the composition of which would support the view that arsenious acid ought to be represented, like phosphorous acid, as a bibasic acid of the formula $2HO.AsHO_2$. No compound of the anhydrous acid with water or its elements has yet, however, been obtained.

The arsenites of potash and soda in solution are sometimes employed as sheep-dipping compositions; and an arsenical soap, composed of, arsenite

potash, soap, and camphor, is used by naturalists to preserve the skins animals. Arsenite of soda is also occasionally employed for preventing crustations in steam-boilers, being prepared for that purpose by dissolving qs. of arsenious acid in 1 eq. of carbonate of soda.

Scheele's green is an arsenite of copper ($2CuO . HO . AsO_3$) prepared by olving arsenious acid in a solution of carbonate of potash, and decomposing the arsenite of potash thus produced by adding sulphate of copper, n the arsenite of copper is precipitated. This poisonous colour is used mpart a bright green tint to paper-hangings, and is sometimes injurious he health of the occupants of rooms thus decorated, since the arsenite opper is often easily rubbed off the paper, and diffused through the n the form of a fine dust, a small portion of which is inhaled with y breath.

he presence of the arsenite of copper in a sample of such paper is readily proved aking it in a little ammonia, which dissolve the arsenite of copper to a liquid, the presence of arsenic in h may be shown by acidifying it a little pure hydrochloric acid, and ng with one or two strips of pure er, which will become covered with el-grey coating of arsenide of cop- On washing the copper, drying it lter-paper, and heating it in a small (fig. 212), the arsenic will be con- ed into arsenious acid, which will sit in brilliant octahedral crystals on cool part of the tube. It is obvious , to avoid mistakes, the ammonia, hy- hloric acid, and copper should be examined in precisely the same way, without suspected paper, so as to render it certain that the arsenic is not derived from them.

Fig. 212.

The effective green colour of the arsenite of copper also leads to its ployment as a colour for feathers, muslin, &c., where it is very injus to the health of the work-people. It has even been ignorantly or dessly used for colouring twelfth-cake ornaments, &c.

n quantities short of poisonous doses, arsenious acid appears to have a arkable effect upon the animal body. Grooms occasionally employ it mprove the appearance of horses, and in Styria it seems to be taken men and women for the same purpose, apparently favouring the secre- of fat. It is said that a continuance of the custom developes a ing for this drug, and enables large doses to be taken without immee danger, though the ultimate consequences are very serious.

olution of arsenite of potash (*Fowler's solution*) has long been used in licine.

76. *Arsenic acid.*—This acid has acquired great importance in the mical arts during the last few years, having been employed to replace expensive tartaric acid used in calico-printing, and to furnish, by its on upon aniline, the magnificent dye known as *Magenta*.

rsenic acid is prepared by oxidising arsenious acid with three-fourths s weight of nitric acid of sp. gr. 1·35, when it dissolves with evolution uch heat and abundant red fumes of nitrous acid—

$$AsO_3 + HO.NO_5 + 2HO = NO_2 + 3HO.AsO_5.$$

r cooling, the solution deposits very deliquescent prismatic crystals *aining* $3HO.AsO_5 + Aq$. When these are heated to 212° F. they

melt, and the liquid gradually deposits needle-like crystals of trihydrated arsenic acid, $3HO.AsO_5$, corresponding to common or tribasic phosphoric acid. At 300° F. the hydrate $2HO.AsO_5$ may be obtained, and at a temperature of 500° F. a white mass of anhydrous arsenic acid (As_2O_5) is left. If this be heated to redness, it fuses and is decomposed into arsenious acid and oxygen.

The hydrates of arsenic acid have acquired unusual importance, in consequence of a costly trial, in the law courts, of the question, whether a patent for Magenta dye could be pronounced invalid because the patentee had described it as being producible by the action of *dry* arsenic acid upon aniline; whereas the *anhydrous* acid, acting upon aniline, will furnish the colour, though either of the solid (and therefore *dry* in popular language) hydrates will do so. The patent was eventually invalidated, though not merely upon this question.

Anhydrous arsenic acid has very much less attraction for water than the anhydrous phosphoric acid to which it corresponds; it deliquesces slowly in air, and dissolves rather reluctantly in water. Neither does it appear that its combinations with water differ from each other, like the phosphoric acids, in the salts to which they give rise, arsenic acid forming tribasic salts only, like common phosphoric acid. The arseniates correspond very closely to the tribasic phosphates with which they are isomorphous (*i. e.*, identical in crystalline form). Thus the three arseniates of soda are similar in composition to the three tribasic phosphates of soda, their formulæ being—

$3NaO.AsO_5$	+	24Aq.
$2NaO.HO.AsO_5$	+	24Aq.
$NaO.2HO.AsO_5$	+	Aq.

But if the two last salts be heated, they lose their basic water without giving rise to new salts corresponding to the pyrophosphate and metaphosphate of soda, and resume their former condition when placed in contact with water.

The common arseniate of soda ($2NaO.HO.AsO_5 + 14Aq.$) is largely used by calico-printers as a substitute for the dung-baths formerly employed, since, like the common phosphate of soda, it possesses the feebly alkaline properties required in that particular part of the process. It is manufactured by combining arsenious acid with soda, and heating the resulting arsenite of soda with nitrate of soda, from which it acquires oxygen, becoming converted into arseniate of soda.

Arsenic acid is a much more powerful acid than arsenious acid, being comparable, in this respect, with phosphoric acid. It appears to be less poisonous than arsenious acid.

177. *Arsenietted hydrogen.*—The only compound of arsenic and hydrogen, the existence of which has been satisfactorily established, is that which corresponds to ammonia and phosphuretted hydrogen gas, and is represented by the formula, AsH_3. It is prepared by the action of sulphuric acid diluted with three parts of water upon the arsenide of zinc obtained by heating equal weights of zinc and arsenic in an earthen retort; $Zn_3As + 3(HO.SO_3) = AsH_3 + 3(ZnO.SO_3)$. The gas is so poisonous in its character that its preparation in the pure state is attended with danger. It has a sickly alliaceous odour, and may be liquefied at -40° F. It is inflammable, burning with a peculiar livid flame, pro

ter and fumes of arsenious acid; $AsH_3 + O_6 = AsO_3 + 3HO$.
interest attaching to this gas depends upon the circumstance
oduction allows of the detection of very minute quantities of
cases of poisoning.

ication of this test, known as Marsh's test, is the safest method of prepar-
ted hydrogen in order to study its properties, for it is obtained so largely
h free hydrogen that it ceases to be so very dangerous. Some fragments
ted zinc are introduced into a half-pint bottle
rovided with a funnel-tube (A), and a narrow tube
right angles and drawn out to a jet at the extremity;
ould be made of German glass, so that it may not
The bottle having been about one-third filled
a little diluted sulphuric acid is poured down the
so as to cause a moderate evolution of hydrogen,
bout five minutes (to allow the escape of the air)
en is kindled at the jet. If a few drops of a solu-
ed by boiling arsenious acid with water be now
n the funnel, arsenietted hydrogen will be evolved
th the hydrogen—

Fig. 213.

$$+ 6(HO.SO_3) = AsH_3 + 6(ZnO.SO_3) + 3HO.$$

en flame will now acquire the livid hue above referred to, and a white
senious acid will rise from it. If a piece of glass or
depressed upon the flame (fig. 214), it will acquire
ooking coating of arsenic, just as carbon would be
om an ordinary gas-flame. Arsenietted hydrogen
ecomposed by heat, so that if the glass tube
ich it passes be heated with a spirit-lamp (fig. 215),
or of arsenic will be deposited a little in front of the heated part, and
the gas will lose its livid hue. These
arsenic are extremely thin, so that a
e quantity of arsenic is required to
thus rendering the test one of extra-
licacy. It must be remembered, how-
oth sulphuric acid and zinc are liable
rsenic, so that erroneous results may
ly arrived at by this test in the hands
hose specially devoted to such investi-

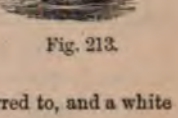


Fig. 214.

Fig. 215.

ed hydrogen, like sulphuretted hydro-
dark precipitates in many metallic

ition of arsenietted hydrogen.—
fic gravity of this gas has been
be 2·695. The formula AsH_3
esent 1 vol. of arsenic vapour and 6 vols. of hydrogen (O = 1 vol.)

Weight of 1 vol. (sp. gr.) of arsenic vapour,	10·600
„ 6 vols. of hydrogen (·069 × 6),	·414
	11·014

um of these is evidently four times the weight of 1 vol. of
hydrogen, hence the formula AsH_3 represents 4 vols. of this
ning 1 vol. of arsenic vapour and 6 vols. of hydrogen.
cular formula ought strictly to be written AsH_6, but, as in the
osphuretted hydrogen, the formula AsH_3 is preferred, in order
a correspondence in composition to ammonia (see also p. 244).
ıretted hydrogen, arsenietted hydrogen, and ammonia, constitute
hydrogen compounds having certain properties in common,

which distinguish them from the compounds of hydrogen with other elements.

Two volumes of each of these gases contain three volumes of hydrogen.

They are all possessed of peculiar odours, that of ammonia being most powerful, and that of arsenietted hydrogen the least.

Ammonia is powerfully alkaline, phosphuretted hydrogen exhibits some tendency to play an alkaline part, whilst arsenietted hydrogen is devoid of alkaline disposition.

All these are inflammable, ammonia being the least so of the gases, and all are decomposed by heat, ammonia least easily and arsenietted hydrogen most easily.

They are all producible from their corresponding oxygen compounds, viz., NO_3, PO_3, and AsO_3, by the action of nascent hydrogen (*e.g.*, contact with zinc and diluted sulphuric acid).

All three are the prototypes of various organic bases which contain some compound radical in place of the hydrogen, thus—

NH_3 is the prototype of		triethylamine,	$N(C_4H_5)_3$
PH_3	,, ,,	triethylphosphine,	$P(C_4H_5)_3$
AsH_3	,, ,,	triethylarsine,	$As(C_4H_5)_3$.

178. *Terchloride of arsenic.*—Only one compound of chlorine with arsenic ($AsCl_5$) has yet been obtained; the chloride corresponding to pentachloride of phosphorus remains to be discovered.* The terchloride may be formed by the direct union of its elements, but the simplest laboratory process for procuring it consists in heating arsenious acid in dry chlorine gas, in a tubulated retort (A, fig. 216), extemporised from a Florence flask (see p. 95.) The arsenious acid soon melts, and the terchloride of arsenic distils over, leaving a melted mass in the flask which forms a brilliantly transparent glass on cooling, the composition of which varies somewhat with the temperature employed, but appears to be essentially $2AsO_3 . AsO_5$. The same vitreous compound may be obtained by fusing arsenious and arsenic acids together. The formation of the terchloride of arsenic may be represented by the equation, $11AsO_3 + Cl_5 = 2AsCl_3 + 3(2AsO_3 . AsO_5)$.

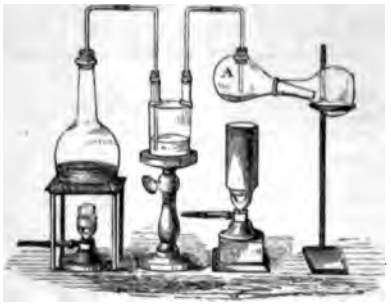


Fig. 216.

Terchloride of arsenic bears a great general resemblance to terchloride of phosphorus; it is a heavy (sp. gr. 2·2), pungent, fuming liquid, decomposed by the moisture of the air, its vapours depositing a white coating of arsenious acid upon the objects in its immediate neighbourhood. When poured into water it deposits arsenious acid; $AsCl_3 + 3HO = AsO_3 + 3HCl$; but when dissolved in the smallest possible quantity of water, it deposits crystals of the formula $AsO_2Cl . 2HO$.

When arsenious acid is dissolved in hydrochloric acid, terchloride of arsenic is formed, $AsO_3 + 3HCl = AsCl_3 + 3HO$, and remains undecomposed by the water in the presence of strong hydrochloric acid, but if water be added, arsenious acid is precipitated. When the solution of arsenious acid in hydrochloric acid is distilled, the terchloride of arsenic distils over, and this is sometimes a convenient method of separating arsenic from articles of food, &c., in testing for that poison. When heated in dry hydrochloric acid gas, arsenious acid yields a glassy compound, which contains $2AsO_3 . AsClO_2$; $3AsO_3 + HCl = 2AsO_3 . AsClO_2 + HO$.

In composition by volume, the terchloride of arsenic resembles terchloride of

* Nicklés appears to have succeeded in forming the pentachloride by the action of hydrochloric acid gas on arsenic acid in presence of ether; he describes it as very unstable, and easily converted into the terchloride.

horus, containing 1 vol. of arsenic vapour, and 6 vols. of chlorine condensed vols., the specific gravity of its vapour being 6·3.
bromide of arsenic much resembles the terchloride in its chemical characters, a solid crystalline substance, easily fusible.

. *Teriodide of arsenic* (AsI_3) is remarkable for not being decomposed by water, he corresponding phosphorus compound. When obtained by heating arsenic dine together, it sublimes in brick-red flakes, which, if prepared on a large scale, in long laminæ like sea-weed. It may be dissolved in boiling water, and allises out unchanged. It may even be prepared by heating 3 parts of arsenic 10 of iodine and 100 of water, when the solution deposits red crystals of the ated teriodide, from which the water may be expelled by a gentle heat.
e *terfluoride of arsenic* (AsF_3) resembles the terchloride, but is much more ile. It may be obtained by distilling 4 parts of arsenious acid with 5 of fluor- and 10 of strong sulphuric acid in a leaden retort (see p. 177). It does not k glass unless water be present, which decomposes it into arsenious and hydro- ic acids.

30. SULPHIDES OF ARSENIC.—There are three well-known sulphides of nic, having the composition AsS_2, AsS_3, and AsS_5, the two former g found in nature.
ealgar, or *bisulphide of arsenic* (AsS_2), is a beautiful mineral, crystal- l in orange-red prisms; but the *red orpiment* used in the arts is gene- prepared by heating a mixture of arsenious acid and sulphur, when hurous acid escapes, and an opaque mass of realgar is left—

$$2AsO_3 + S_7 = 2AsS_2 + 3SO_2.$$

nother process for preparing it consists in distilling arsenical pyrites i iron pyrites—

$FeS_2 . FeAs$	+	$2FeS_2$	=	$4FeS$	+	AsS_2.
Arsenical pyrites.		Iron pyrites.		Sulphide of iron.		Realgar.

he realgar distils over, and condenses to a red transparent solid. lgar burns in air with a blue flame, yielding arsenious acid and sul- rous acid. If it be thrown into melted saltpetre, it burns with a iant white flame, being converted into arseniate and sulphate of sh. This brilliant flame renders realgar an important ingredient in *an fire* and similar compositions for fire-works and signal-lights. A ture of one part of red orpiment with 3·5 parts of sublimed sulphur 14 parts of nitre is used for signal-light composition.

algar is not easily attacked by acids; nitric acid, however, dissolves it, with id of heat, forming arsenic acid and sulphuric acid, with separation of part of ulphur in the free state. Alkalies (potash, for example) partly dissolve it, ng a brown substance, which appears to be a subsulphide of arsenic (As_6S).

ellow orpiment, or *tersulphide of arsenic* (AsS_3), is found native in w prismatic crystals. The paint known as *King's yellow* is a mix- of tersulphide of arsenic and arsenious acid, prepared by subliming a ure of sulphur with arsenious acid—

$$S_9 + 2AsO_3 = 2AsS_3 + 3SO_2.$$

of course, very poisonous.

is substance, like realgar, is not much affected by acids, excepting nitric acid; t dissolves entirely in potash, forming arsenite of potash and *sulpharsenite* of hide of) potassium; $6KO + 2AsS_3 = 3KS . AsS_3 + 3KO . AsO_3$. Ammonia dissolves it easily, forming a colourless solution which is employed for dyeing w, since if a piece of stuff be dipped into it and exposed to air, the ammonia *olatilise, leaving the yellow orpiment* behind.

The formation of the characteristic yellow tersulphide is turned to account in testing for arsenic; if a solution prepared by boiling arsenious acid with distilled water be mixed with a solution of hydrosulphuric acid, a bright yellow liquid is produced, which looks opaque by reflected, but transparent by transmitted light, and may be passed through a filter without leaving any solid matter behind. This solution probably contains a soluble compound of tersulphide of arsenic with hydrosulphuric acid ($8HS . AsS_3$); it is, however, very unstable, being decomposed by evaporation, with precipitation of the tersulphide. The addition of a little hydrochloric acid, or of sal-ammoniac, and many other neutral salts, will also cause a separation of the tersulphide from this solution; even the addition of a hard water will have that effect. If the solution of arsenious acid be acidified with hydrochloric acid before adding the hydrosulphuric acid, the bright yellow tersulphide of arsenic is precipitated at once, and may be distinguished from any other similar precipitate by its ready solubility in solution of carbonate of ammonia.

From its combining readily with the alkaline sulphides to form soluble compounds, the tersulphide of arsenic is often called *sulpharsenious acid*.

Pentasulphide of arsenic (AsS_5), or *sulpharsenic acid*, possesses far less practical importance than the preceding sulphides; it may be obtained by fusing the tersulphide with sulphur, when it forms an orange-coloured glass, easily fusible, and capable of being sublimed without change. When hydrosulphuric acid gas is passed through solution of arsenic acid, a white precipitate of sulphur is first obtained, the hydrogen reducing the arsenic acid to arsenious acid; $AsO_5 + 2HS = AsO_3 + 2HO + S_2$; and if the passage of the gas be continued, the arsenious acid is decomposed, and tersulphide of arsenic is precipitated; these changes are much accelerated by heat. But if a solution of arseniate of soda be saturated with hydrosulphuric acid, it is converted into sulpharseniate of (sulphide of) sodium—

$$2NaO . HO . AsO_5 + 7HS = 8HO + 2NaS . AsS_5 .$$

On adding hydrochloric acid to this solution, a bright yellow precipitate of pentasulphide of arsenic is obtained—

$$2NaS . AsS_5 + 2HCl = 2NaCl + 2HS + AsS_5 .$$

Pentasulphide of arsenic is one of the most powerful of the sulphur acids; it expels hydrosulphuric acid from its combinations with the alkaline sulphides, and is capable of forming with these, sulpho-salts, containing respectively one, two, and three equivalents of the alkaline sulphide, which may be obtained by the action of hydrosulphuric acid upon the corresponding arseniates.

GENERAL REVIEW OF THE NON-METALLIC ELEMENTS.

181. At the conclusion of the history of the non-metals, it may be well to call attention to the points of resemblance which classify them into separate groups or families, most of which are connected, by some analogies, with one or more members of the class of metals.

Hydrogen stands alone among the non-metals, its chemical properties and functions being widely different from those of any other non-metal, but connecting it very closely with the most highly electropositive (or *basylous*) metals, such as potassium and sodium.

Oxygen, *Sulphur*, *Selenium*, and *Tellurium* compose a group, the members of which (in the state of vapour) combine with twice their volume of hydrogen to form compounds which (in the state of vapour) occupy the same volume as the hydrogen occupied before combination. All these hydrogen compounds are capable of playing a feebly acid part, and their hydrogen may be displaced by an equivalent weight of a metal to produce compounds exhibiting a general agreement in chemical properties. This group is connected with the metals through tellurium, not only by its physical properties, but by its forming an oxide (TeO_2), which occasionally acts as a weak base.

trogen, *Phosphorus*, and *Arsenic* are connected together by the gene-
nalogy of their hydrogen and oxygen compounds, the two last mem-
of the group being far more closely connected with each other than
nitrogen. With the metals, they are connected through arsenic, the
ogen compound of which is very similar in properties, and probably in
osition, to antimonietted hydrogen ; arsenious acid (AsO_3) is also cap-
of occupying the place of teroxide of antimony (SbO_3) in certain salts
at oxide; and the sulphides of antimony correspond in composition, and
me of their properties, to those of arsenic. One form of arsenious
(the prismatic) is isomorphous with native oxide of antimony, and
oxide may be obtained in octahedra, the ordinary form of arsenious
so that these oxides are *isodimorphous*.
ese elements are also connected with the oxygen group through
ur, selenium, and tellurium, the relations of which to hydrogen and
metals are somewhat similar to those of phosphorus and arsenic.
rbon, *Boron*, and *Silicon* resemble each other in their allotropic
s, their resistance to fusion and volatilisation, and their forming
e acids with oxygen. To the metals they are allied through silicon,
h resembles tin in the composition and character of its oxide and
ide.
is group is connected with the nitrogen group through boron, for
ic acid resembles arsenious acid in its tribasic character, and its
ing vitreous compounds with the alkalies. In certain compounds
ic and arsenious acids are interchangeable.
lorine, *Bromine*, *Iodine*, and *Fluorine* are intimately connected by
erous analogies, which have been already pointed out (p. 182). Some
e properties of iodine, as its relations to oxygen, and the solubility
terchloride in water, connect it slightly with the metals, whilst the
al correspondence in composition between the chlorides and the
es, allies this group to the oxygen group of non-metallic elements.
the non-metals be classified according to their atomicities (see p. 151),
ll be found that, with only few exceptions, the classification will
ide with that founded upon their chemical analogies in other respects.
, the members of the oxygen group are all diatomic, or capable of
ining with two atoms of hydrogen, as shown by the molecular for-
e of their hydrogen compounds, H_2O, H_2S, H_2Se, H_2Te. The
gen group is generally represented as triatomic (though, from our
nt knowledge of the vapour densities of phosphorus and arsenic,
elements are strictly hexatomic), their hydrogen compounds being
, PH_3, and AsH_3. Boron is also a triatomic element, for, in BCl_3,
oron occupies the place of three atoms of hydrogen.
rbon and silicon, however, are tetratomic elements, as shown in
h-gas, CH_4, and in chloride of silicon, $SiCl_4$.
lorine, bromine, iodine, and fluorine are monatomic, their hydrogen
ounds having the molecular formulæ, HCl, HBr, HI, and HF.
e atomicity of an element is sometimes expressed in a formula by a
or dashes, placed above and to the right of the element ; thus the
ols, Cl', O'', N''', C'''', indicate the respective atomicities of those
nts. When the atomicity of an element is taken into account, it
to explain the constitution of compounds which would otherwise
r quite anomalous. For example, there is a compound of the mole-
formula, N_3H_6P, obtained by the action of terchloride of pho
s upon ammonia ; recollecting the triatomic character of phosphor

we perceive this compound to represent three molecules of ammonia (N_3H_9), in which phosphorus is the substitute for three atoms of hydrogen, which is at once expressed if the formula be written, $N_3H_9P^{v}$. Again, chlorocarbonic acid, $\Theta\Theta Cl_2$, appears an inexplicable association of elements, until the tetratomic character of carbon and diatomic character of oxygen are taken into account, as in the formula $\Theta''''\Theta''Cl'_2$, when it appears that the diatomic oxygen and the two atoms of monatomic chlorine are the substitutes for four atoms of hydrogen in marsh-gas, ΘH_4, and it might plausibly be given as a reason why the apparently indifferent carbonic oxide should combine with chlorine, that the atomicity of the carbon is only partly satisfied in carbonic oxide, which contains only oxygen equal in value to two atoms of hydrogen, the tetratomic carbon requiring the value of two more atoms of hydrogen to complete the compound atom. In carbonic acid, $\Theta''''\Theta''_2$, the two atoms of diatomic oxygen fully complete the compound.

In a similar manner the absorption of carbonic oxide by subchloride of copper may be explained; for the atomic formula of that salt is $Cu'Cl'$, and hence it is capable of supplying the two absent atoms in $\Theta''''\Theta''$.

Many more examples of the same kind might be gathered from the preceding pages, but these will probably be sufficient to mark the importance of remembering the atomicities of the elements in speculative chemistry; indeed, without this clue it is impossible to find any meaning whatever in a very large number of the formulæ of organic substances, whilst with it, not only their constitution, but in many cases their mode of formation, becomes as intelligible as that of the simplest mineral compounds.

CONSTITUTION OF SALTS.

182. The term *salt*, like *acid* and *alkali*, was, of course, purely empirical in its origin, being conferred upon every solid substance which exhibited any of the prominent characters of sea-salt (sal, *brine*, *σάλος*, *the sea*), such as solubility in water and tendency to crystallisation.

When the great mass of chemical facts accumulated by the alchemists, metallurgists, and apothecaries, came to be classified, and the distinction between acids and bases was recognised, the term salt was extended to all those substances, such as *muriate of soda*, nitrate of potash, carbonate of lime, &c., from which a base and an acid could be obtained, without regard to their solubility or tendency to crystallise. When the analytical powers of the chemist were more fully developed, it was found that muriate of soda and a large class of similar salts did not contain an acid and a base, but that these substances were *produced* and not *educed* from the salts by the chemical operations to which they were subjected. Thus muriate of soda, from which muriatic acid had been so easily *produced* by the action of sulphuric acid, was shown to contain only sodium and chlorine.

This led to a classification of salts into *haloid* salts (*ἅλς*, *the sea*), or those composed, like chloride of sodium, of a metal combined with a salt radical or halogen, and *oxy-acid* salts, or those composed of a metallic oxide combined with an oxygen acid. (It will have been remarked that the tendency of modern chemistry is to represent this second class of salts by formulæ which do not admit the existence of the metal as an oxide in *the salt.*)

pendently of all differences of opinion with respect to the actual ution of salts, the criterion by which the claims of a substance to le can be estimated is this: *a salt is a compound which may be by the action of an acid upon a base*, water, which is a very general of such action, being excepted.

oxy-acid salts soon came to be divided into *neutral* and *acid* salts, ing to their effect upon vegetable colours and the organ of taste, class of *basic* salts was afterwards added when it was found that a soluble salt sometimes became insoluble by combining with an nal quantity of base.

her investigation has shown that the neutral taste of a salt, and its lity to test-papers, depend less upon the proportions of the acid and hich are contained in it, than upon the chemical energy of these nces.

s, *potash* combined with 1 eq. of *sulphuric acid* forms a salt which fectly neutral to taste and to litmus-papers, whilst with 1 eq. of *ic acid* it forms a strongly alkaline salt; and 1 eq. of *sulphuric* mbined with 1 eq. of *oxide of zinc* forms a salt which is strongly test-papers.

lt may, therefore, be neutral in chemical constitution, and acid or e in reaction to test-papers, and it has been proposed to employ the *ormal* to designate those salts which are neutral in chemical con- n, and to restrict the term neutral to those salts which are neither r alkaline to test-papers. Thus, sulphate of potash would be both ral and a normal salt, whilst sulphate of zinc and carbonate of are normal, but not neutral salts.

ormal salt is one in which the oxygen contained in the base bears in proportion to the oxygen contained in the acid, this proportion fixed for each acid.

s, a normal carbonate is one in which the oxygen of the base bears oxygen of the acid the ratio of 1 : 2, as in normal carbonate of , $KO.CO_2$.

ormal sulphate is one in which the oxygen of the base bears to the n of the acid the ratio of 1 : 3, as in normal sulphate of zinc SO_3.

form a normal salt with a sesquioxide, 3 eqs. of sulphuric acid are d. Thus the sulphate of alumina, $Al_2O_3 . 3SO_3$, although powerfully test-papers, is a normal sulphate, for the oxygen of the base bears oxygen of the acid the ratio of 1 : 3.

cid salt is one in which the oxygen in the acid is in greater proportion n the normal ratio. Thus bicarbonate of potash, $KO . HO . 2CO_2$, l in chemical constitution, though alkaline to test-papers, for the n of the base is to the oxygen of the acid as 1 : 4, whilst the normal or carbonates is 1 : 2. Acid salts usually have the deficiency of pplied by water, but not invariably, as in fused borax, $NaO . 2BO_3$, mate of potash, $KO . 2CrO_3$, dried bisulphate of soda, $NaO . 2SO_3$.

asic salt is one in which the oxygen in the base is in greater propor- an in the normal ratio. Thus, white lead, $2(PbO . CO_2)$, $PbO . HO$, sic carbonate, for the oxygen of the base is to the oxygen of the 3 : 4, whereas the normal ratio is 2 : 4 or 1 : 2.

minite, $Al_2O_3 . SO_3 + 9HO$, is a basic salt, for the oxyg se is to the oxygen in the acid as 3 : 3, whilst the normal

The following are the normal ratios for some of the most important classes of salts :—

Salts.	Normal Ratio.	Examples.	
Carbonates,	1 : 2	$NaO.CO_2$	Carbonate of soda.
Borates,	3 : 8?	$3MgO.BO_3$	Borate of magnesia.
Silicates,	2 : 2	$2FeO.SiO_2$	Forge cinder.
Nitrates,	1 : 5	$KO.NO_5$	Saltpetre.
Chlorates,	1 : 5	$KO.ClO$	Chlorate of potash.
Sulphites,	1 : 2	$NaO.SO_2$	Sulphite of soda.
Sulphates,	1 : 3	$CaO.SO_3$	Sulphate of lime.
Metaphosphates,	1 : 3	$NaO.PO_3$	Metaphosphate of soda.
Pyrophosphates,	2 : 5	$2NaO.PO_5$	Pyrophosphate of soda.
Orthophosphates	3 : 5	$3CaO.PO_5$	Bone phosphate of lime.
Arsenites,	3 : 3?	$3AgO.AsO_3$	Arsenite of silver.
Arseniates,	3 : 5	$3CoO.AsO_5$	Cobalt bloom.
Chromates,	1 : 3	$KO.CrO_3$	Chromate of potash.
Permanganates,	1 : 7	$KO.Mn_2O_7$	Permanganate of potash.

In order to explain the above results obtained by the actual analysis of salts, it may be supposed that the salts are formed upon the type of the hydrated acid, and that a normal salt is one in which the water in the hydrated acid is displaced by an equivalent quantity of base; thus, the sulphates are formed upon the type of oil of vitriol, $HO.SO_3$, and the HO must be displaced by KO to form the normal sulphate of potash; but when alumina (Al_2O_3) is employed to displace the water, one-third of the quantity represented by that formula would be equivalent to the HO (for Al_2 is equivalent to H_3), and therefore the normal sulphate of alumina would be $\frac{1}{3}(Al_2O_3).SO_3$, or avoiding the fraction, $Al_2O_3.3SO_3$.

Binary theory of the constitution of salts.—The circumstance that it is only the hydrogen of the hydrated acid that is displaced by the metal, has given rise to the *binary theory* of salts, according to which all acids and salts are constituted after the type of hydrochloric acid and chloride of sodium; the acid being composed of hydrogen combined with a *compound salt-radical* made up of the other elements present in the acid. Thus, sulphuric acid ($HO.SO_3$) would become H,SO_4 nitric acid, H,NO_6; metaphosphoric acid, H,PO_6; pyrophosphoric, H_2,PO_7; tribasic phosphoric, H_3,PO_8, and their normal salts are formed by the substitution of an equivalent quantity of a metal for the hydrogen; neutral sulphate of potassium would be K,SO_4; pyrophosphate of sodium, Na_2,PO_7; triphosphate of calcium, Ca_3,PO_8. The acid salts would be those in which only part of the hydrogen is displaced by a metal; bisulphate of potassium would become $K,H,2SO_4$, acid pyrophosphate of sodium, Na,H,PO_7. Double salts would be those in which the hydrogen is displaced by different metals; thus, alum ($KO.SO_3$, $Al_2O_3.3SO_3$) would become $K,Al_2,4SO_4$; acid phosphate of potassium and sodium (KO,NaO,HO,PO_5) K,Na,H,PO_8. The serious objection to this view, that it overlooks radicals now existing (as SO_3, PO_5, CO_2), and substitutes others which are not known to exist (as SO_4, PO_8, CO_4) has been already pointed out.

Water-type theory of the constitution of salts.—Another ingenious theory of the constitution of salts is that known as the *water-type* theory, according to which all oxygen acids are fashioned after the type of water,

r the displacement of its hydrogen by a compound radical, such displace-ent being total in the anhydrous acids, and partial in the hydrated acids. o render it possible to show the partial displacement of the hydrogen, ne molecular formula for water, $H_2\Theta$ or $\left.\begin{matrix}H\\H\end{matrix}\right\}\Theta$, must be employed. Then, monobasic acid is formed upon the type of one molecule of water, by ne displacement of one atom of hydrogen to form the (hydrated) acid, and f both atoms to form the (anhydrous acid or) anhydride. Thus nitric cid ($HO.NO_2$) would be written $\left.\begin{matrix}H\\N\Theta_2\end{matrix}\right\}\Theta$, and *nitric anhydride* (NO_2) would become $\left.\begin{matrix}N\Theta_2\\N\Theta_2\end{matrix}\right\}\Theta$; and nitrate of potassium ($KO.NO_2$) would e $\left.\begin{matrix}K\\N\Theta_2\end{matrix}\right\}\Theta$, and a glance at these formulæ shows why a monobasic acid ike nitric acid does not form either acid salts or double salts, because it ontains only one atom of hydrogen, and therefore can only form a single alt with each metal by displacement of that hydrogen. This view does ot ignore the existence of the anhydrous nitric acid, and assumes, as the adical of the acid, the substance $N\Theta_2$, which has the composition of nitric eroxide. The formation of nitric acid by the action of water upon nitric nhydride would be thus expressed—

$$\left.\begin{matrix}H\\H\end{matrix}\right\}\Theta + \left.\begin{matrix}N\Theta_2\\N\Theta_2\end{matrix}\right\}\Theta = \left.\begin{matrix}H\\N\Theta_2\end{matrix}\right\}\Theta + \left.\begin{matrix}N\Theta_2\\H\end{matrix}\right\}\Theta.$$

In a similar manner, phosphoric anhydride (PO_2) would be represented y $\left.\begin{matrix}P\Theta_2\\P\Theta_2\end{matrix}\right\}\Theta$, metaphosphoric acid ($HO.PO_2$) by $\left.\begin{matrix}H\\P\Theta_2\end{matrix}\right\}\Theta$, and the meta-hosphate of sodium by $\left.\begin{matrix}Na\\P\Theta_2\end{matrix}\right\}\Theta$. In this case, however, the radical $P\Theta_2$, so far as we know, imaginary.

A bibasic acid is one which is composed after the type of a double olecule of water, $\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}\Theta_2$ and therefore contains two atoms of hydro-n which may be displaced either entirely by a metal, yielding a normal lt, or partly by a metal, yielding an acid salt, or by two metals, yielding double salt. For example, sulphuric acid ($HO.SO_2$) would be $\left.\begin{matrix}H_2\\S\Theta_2''\end{matrix}\right\}\Theta_2$, or two molecules of water, in which two atoms of hydrogen re displaced by the diatomic radical $S\Theta_2$; normal sulphate of potassium $\left.\begin{matrix}K_2\\S\Theta_2''\end{matrix}\right\}\Theta_2$, acid sulphate of potassium (bisulphate of potash) $\left.\begin{matrix}KH\\SO_2''\end{matrix}\right\}\Theta_2$ nd sulphuric anhydride, $\left.\begin{matrix}S\Theta_2''\\S\Theta_2''\end{matrix}\right\}\Theta_2$.

Here again the radical $S\Theta_2$ has the same composition as sulphurous cid, which might well be accepted as the radical of sulphuric acid.

Again, carbonic anhydride would be $\left.\begin{matrix}C\Theta''\\C\Theta''\end{matrix}\right\}\Theta_2$, the imaginary carbonic cid, $\left.\begin{matrix}H_2\\C\Theta''\end{matrix}\right\}\Theta_2$, carbonate of potassium, $\left.\begin{matrix}K_2\\C\Theta''\end{matrix}\right\}\Theta_2$, acid carbonate of potas-ium, $\left.\begin{matrix}KH\\C\Theta''\end{matrix}\right\}\Theta_2$, carbonate of potassium and sodium, $\left.\begin{matrix}KNa\\C\Theta''\end{matrix}\right\}\Theta_2$

The radical of carbonic acid, therefore ($\overset{\cdot\cdot}{C}\Theta$), would have the same composition as carbonic oxide, which is seen to have a diatomic character in its compound with chlorine, $\overset{\cdot\cdot}{C}\Theta''Cl_2$, where it occupies the place of two atoms of hydrogen.

In applying this view to pyrophosphoric acid ($2HO . PO_5 = H_2PO_7$), some difficulty arises because its molecular formula cannot be written on the type of two molecules of water ($H_4\Theta_2$) on account of the indivisibility of the O_7 into two whole numbers; it is therefore necessary to take four molecules of water as the type, when we have—

Type, $\left.\begin{matrix}H_4\\H_4\end{matrix}\right\}\Theta_4$, pyrophosphoric acid, $\left.\begin{matrix}H_4\\(P_2\Theta_3)''''\end{matrix}\right\}\Theta_4$, pyrophosphate of sodium, $\left.\begin{matrix}Na_4\\(P_2\Theta_3)''''\end{matrix}\right\}\Theta_4$, acid pyrophosphate of sodium, $\left.\begin{matrix}Na_2H_2\\(P_2\Theta_3)''''\end{matrix}\right\}\Theta_4$.

Here the increased complexity of the formulæ appears objectionable.

A few salts are known in which two acids are combined with the same base, such as the acetonitrate of baryta ($BaO . NO_5$, $BaO . C_4H_3O_3$), composed of nitrate and acetate of baryta.

It is obvious that the same reasoning which leads to the conclusion that an acid capable of forming a double salt with two different bases is dibasic, or contains a diatomic acid radical, would also support the inference that a base capable of forming a double salt with two different acids is di-acid, or contains a diatomic basic radical. Hence the existence of the above acetonitrate of baryta countenances the belief that barium is a diatomic metal. The formula of the salt would then be written, on the type of two molecules of water, thus—$\left.\begin{matrix}Ba''\\(C_2H_3\Theta)'\\(N\Theta_3)'\end{matrix}\right\}\Theta_2$

A tribasic acid is formed upon the type of a treble molecule of water, thus—

Type, $\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}\Theta_3$, tribasic phosphoric acid, $\left.\begin{matrix}H_3\\P\Theta'''\end{matrix}\right\}\Theta_3$, triphosphate of sodium, $\left.\begin{matrix}Na_3\\P\Theta'''\end{matrix}\right\}\Theta$, common phosphate of sodium, $\left.\begin{matrix}Na_2H\\P\Theta'''\end{matrix}\right\}\Theta_3$, microcosmic salt (phosphate of sodium and ammonium), $\left.\begin{matrix}Na(NH_4)'H\\P\Theta'''\end{matrix}\right\}O_3$.

But in this case also an unknown radical, $P\Theta$, is assumed.

Many chemists now represent the acids and salts by their molecular formulæ, without insisting upon their containing any definite compound radical, or being composed upon any particular type. Thus nitric acid is written $HN\Theta_3$, without expressing an opinion as to the existence of $N\Theta_3$ as an actual entity.

The following definitions are relied upon by those who adopt this course:—

An *acid* is a compound containing hydrogen, the whole or part of which is displaceable by a metal.

A *salt* is a compound derived from an acid by the displacement of hydrogen by a metal.

A *monobasic acid* contains but one atom of displaceable hydrogen, and therefore can only form one series of salts.

A *dibasic acid* contains two atoms of displaceable hydrogen, and there can form two series of salts (normal and acid salts).

A *tribasic acid* contains three atoms of displaceable hydrogen, &c.

can form three series of salts (normal salts, and two series of).

nal salt is one in which the whole of the displaceable hydrogen displaced by a metal.

id salt is one in which only part of the displaceable hydrogen displaced by a metal.

ble salt is one in which the displaceable hydrogen has been dis- different metals.

e salt is a combination of a salt with a basic oxide.

examples may be collected here to illustrate these definitions :—

Monobasic Acids and Salts.

ic acid,	$HN\Theta_3$
ate of potassium,	$KN\Theta_3$
aphosphoric acid,	$HP\Theta_3$
aphosphate of sodium,	$NaP\Theta_3$
ophosphorous acid,	$HPH_2\Theta_2$
ophosphite of sodium,	$NaPH_2\Theta_2$

Dibasic Acids and Salts.

huric acid,	$H_2S\Theta_4$
mal sulphate of potassium,	$K_2S\Theta_4$
l „ „	$KHS\Theta_4$
sphorous acid,	$H_2PH\Theta_3$
mal phosphite of sodium,	$Na_2PH\Theta_3$
l phosphite of barium,	$BaHPH\Theta_3$

Tribasic Acids and Salts.

ophosphoric acid,	$H_3P\Theta_4$
mal orthophosphate of sodium,	$Na_3P\Theta_4$
acid orthophosphate (or common phosphate),	$Na_2HP\Theta_4$
id orthophosphate,	$NaH_2P\Theta_4$
ocosmic salt,	$Na(NH_4)HP\Theta_4$
nic acid,	$H_3As\Theta_4$
mal arseniate of sodium,	$Na_3As\Theta_4$
acid arseniate „	$Na_2HAs\Theta_4$
id arseniate „	$NaH_2As\Theta_4$

view of the constitution of acids and salts, it may be objected esupposes the existence of a hydrogen compound corresponding ition to the normal salt. Thus the carbonates would be derived imaginary carbonic acid of the formula $H_2C\Theta_3$; the arsenites imaginary arsenious acid, $H_3As\Theta_3$, &c. It must, however, be dged that no theory of the constitution of acids and salts has advanced which is thoroughly supported on all sides by experi- idence.

what has been stated above, it will have been seen that an ion of the acid itself is by no means necessary in order to ascer- its *basicity* is. If only one series of its salts can be discovered, nobasic acid. If a normal and an acid salt (or a double salt) tained, the acid is dibasic. When, beside the normal salt, ther- *ries of acid salts, the acid* is tribasic.

CHEMISTRY OF THE METALS.

183. The general principles of chemistry having been explained a illustrated in the history of the non-metallic elements, the chemistry the metals will be discussed with less attention to details, wh however interesting in a strictly chemical sense, are not, at present, immediate practical importance.

The definition of a metal has been already given at p. 11, as *an elem capable of forming a base by union with oxygen.*

POTASSIUM.

The indispensable alkali, *potash*, appears to have been originally deriv from the granitic rocks, where it exists in combination with silicic a and alumina, in the well-known minerals, *feldspar* and *mica*. These ro having, in course of time, disintegrated to form soils for the support plants, the potash has been converted into a soluble state, and has pass into the plants as a necessary portion of their food.

In the plant, the potash is found to have entered into various forms of combination; thus, most plants contain sulphate of potash and chloride of potassium; but the greater portion of the potash exists in combination with certain vegetable acids formed in the plant, and when the latter is burnt, the salts of potash with the vegetable acids are decomposed by the heat, leaving the potash in combination with carbonic acid, forming carbonate of potash ($KO.CO_2$).

Carbonate of potash.—When the ashes of plants are treated with water, the salts of potash are dissolved, those of lime and magnesia being left. On separating the aqueous solution and evaporating it to a certain point, a great deal of the sulphate of potash, being much less soluble, is deposited, and the carbonate of potash remains in the solution; this is evaporated to dryness, when the carbonate of potash is left, mixed with much chloride of potassium, and some sulphate of potash; this mixture constitutes the substances imported from America and other countries where wood is abundant, under the name of *potashes*, which are much in demand for the manufacture of soap and glass. When further purified, these are sold under the name of *pearlash*, but this is still far from being pure carbonate of potash.

During the fermentation of the grape-juice, in the preparation of wine, hard crystalline substance is deposited, which is known in commerce by he name of *argol*, or when purified, as cream of tartar. The chemical

name of this salt is bitartrate of potash, for it is derived from potash and tartaric acid, a vegetable acid having the composition $2HO.C_8H_4O_{10}$. When this salt ($KO.HO.C_8H_4O_{10}$) is heated, the tartaric acid is decomposed into a variety of products, among which are found carbonic acid, which remains in combination with the potash, and carbon, which is left mixed with the carbonate of potash; but if the heat be continued, and free access of air permitted, the carbon will be entirely burnt away, and carbonate of potash will be left (*salt of tartar*).

In wine-producing countries, carbonate of potash is prepared from the refuse yeast which rises during the fermentation, and is dried in the sun in order to be subsequently incinerated.

The fleeces of sheep contain a considerable proportion of potash combined with an animal acid; when the fleece is washed with water, the salt of potash is dissolved out, and on evaporating the liquid and burning the residue, it is converted into carbonate of potash.

Hydrate of potash.—Carbonate of potash was formerly called potash, and was supposed to be an elementary substance. It was known that its alkaline qualities were rendered far more powerful by treating it with lime, which caused it to be termed *mild* alkali, in order to distinguish it from the *caustic** alkali obtained by means of lime, and possessed of very powerful corrosive properties. Lime, it was said, is derived from limestone by the action of fire, and therefore owes its peculiar properties to the acquisition of a certain amount of the matter of fire, which, in turn, it imparts to the mild alkali, and thus confers upon it a caustic or burning power.

Black's researches in the middle of the eighteenth century, which are often referred to as models of inductive reasoning, exposed the fallacy of this explanation, and proved that instead of acquiring anything from the fire, the limestone actually lost carbonic acid, and instead of imparting anything to the mild alkali, the lime really gained as much carbonic acid as it had previously lost.

The caustic potash, so largely employed by the soap-maker, is obtained by adding slaked lime to a boiling diluted solution of the carbonate of potash, when the water of the hydrate of lime is exchanged for the carbonic acid, and the carbonate of lime is deposited at the bottom of the vessel, whilst *hydrate of potash* remains in the clear solution—

$KO.CO_2$	+	$CaO.HO$	=	$CaO.CO_2$	+	$KO.HO$.
Carbonate of potash.		Hydrate of lime.		Carbonate of lime.		Hydrate of potash.

If the solution of carbonate of potash be too strong, the lime will not remove the whole of the carbonic acid.

When the solution is evaporated, the hydrate of potash remains as a clear oily liquid, which solidifies to a white mass as it cools, and forms the fused potash of commerce, which is often cast into cylindrical sticks for more convenient use.† The hydrate of potash is the most powerful alkaline substance in ordinary use, and is very frequently employed by the chemist on account of its energetic attraction for the different acids. It is generally used in the state of solution, the strength of which is inferred from its specific gravity, this being higher in proportion to the amount of potash contained in the solution.

* From καιω, to burn.

† These have sometimes a greenish colour, due to the presence of some manganate of *potash*.

Potassium.—Of the composition of hydrate of potash nothing was known till the year 1807, when Davy succeeded in decomposing it by the galvanic battery; this experiment, which deserves particular notice, as being the first of a series resulting in the discovery of so many important metals, was made in the following manner:—A fragment of hydrate of potash, which, in its dry state, does not conduct electricity, was allowed to become slightly moist by exposure to the air, and placed upon a plate of platinum attached to the positive (copper) end of a very powerful galvanic battery; when the wire connected with the negative (zinc) end was made to touch the surface of the hydrate of potash, some small metallic globules resembling mercury made their appearance at the extremity of this (negative) wire, at which the hydrogen contained in the hydrate of potash was also eliminated, whilst bubbles of oxygen were separated on the surface of the platinum plate connected with the positive wire (*see* p. 21). By allowing the negative wire to dip into a little mercury contained in a cavity upon the surface of the potash, a combination of potassium with mercury was obtained, and the mercury was afterwards separated by distillation. This process, however, furnished the metal in very small quantities, and, though it was obtained with greater facility a year or two afterwards by decomposing hydrate of potash with white-hot iron, some years elapsed before any considerable quantity of potassium was prepared by the present method of distilling in an iron retort an intimate mixture of carbonate of potash and carbon, obtained by calcining cream of tartar; in this process the oxygen of the potash is removed by the carbon in the form of carbonic oxide ($KO.CO_2 + C_2 = K + 3CO$).

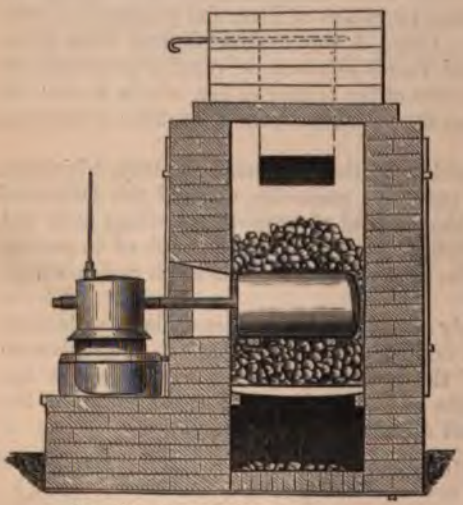


Fig. 217.—Preparation of potassium.

The annexed figure represents the iron retort connected with its copper receiver, surrounded with cold water, and containing petroleum to protect the distilled potassium from oxidation. The lateral tube of the receiver permits the tube of the retort to be cleared, if necessary, during the distillation, by the passage of an iron rod.

Some of the most striking properties of this metal have already been referred to (p. 23); its softness, causing it to be easily cut like wax, the rapidity with which its silvery surface tarnishes when exposed to the air, its great lightness (sp. gr. 0·865), causing it to float upon water, and its taking fire when in contact with that liquid, sufficiently distinguish it from other metals. It fuses easily when heated, and is converted, at a higher temperature, into a green vapour; if air be present, it burns with a violet-coloured flame, and is converted into *anhydrous potash*, the oxide of potassium (KO).

The property of burning with this peculiar violet-coloured flame is

acteristic of potassium, and allows it to be recognised in its com-nds.

f a solution of nitrate of potash (saltpetre) in water be mixed with enough spirit wine to allow of its being inflamed, the flame will have a peculiar lilac colour. is colour may also be developed by exposing a very minute particle of saltpetre, ken on the end of a heated platinum wire, to the reducing (inner) blowpipe flame g. 218), when the potassium, being reduced to the metallic state, and passing

Fig. 218.—Coloured flame test.

into the oxidising (outer) flame in the state of vapour, imparts to that flame a lilac tinge.

The difficulty and expense attending the preparation of potassium have prevented its receiving any application except in purely chemical operations, where its attraction for oxygen, chlorine, and other electronegative elements, is often turned to account.

The *chloride of potassium* (KCl) is an important natural source of this metal, being extracted from sea-water, from kelp (the ash of sea-weed), and from the refuse of the manufacture of sugar from beet-root. It also occurs in combination with chloride of magnesium, forming the mineral known as *carnallite* ($KCl \cdot 2MgCl \cdot 12HO$), an immense saline deposit overlying the rock-salt in the salt-mines of Stassfurth in Saxony. Carnallite resembles rock-salt in appearance, but is very deliquescent; it promises to become the most important source of potassium hitherto discovered.

Bicarbonate of potash ($KO \cdot HO \cdot 2CO_2$), which is much used in medicine, is obtained by passing carbonic acid through a strong solution of carbonate of potash, when it is deposited in crystals, being much less soluble in water than the normal carbonate.

Nitrate of potash ($KO \cdot NO_5$), or *saltpetre*, will be specially considered in the section on gunpowder.

Equivalent and atomic weights of potassium.—The chloride of potassium has been found to contain 35·5 parts by weight (1 eq.) of chlorine and 39 parts of potassium; 39 is therefore regarded as the equivalent weight of this metal. Since this represents the quantity required to displace one atom of hydrogen from its compounds, it is also taken as the atomic weight of potassium. Since potash contains 39 potassium combined with 8 oxygen, its atomic formula would be $K_2\Theta$ ($\Theta = 16$); and hydrate of potash would be $KH\Theta$. Chloride of potassium, however, has the atomic formula KC corresponding with its equivalent formula, because the atomic weights of both its elements are the same as their equivalent weights.

The following less important compounds of potassium have not been noticed e

where, and are not of sufficient practical importance to require particular descri in this work :—

Binoxide of potassium,		KO_2	Tersulphide of potassium,		K
Peroxide	,,	KO_4	Tetrasulphide	,,	K
Sulphide	,,	KS	Pentasulphide	,,	K
Bisulphide	,,	KS_2			

SODIUM.

184. Sodium is often found, in place of potassium, in the felds other minerals, but we are far more abundantly supplied with it form of *common salt* (chloride of sodium, NaCl), occurring not only solid state, but dissolved in sea-water, and in smaller quantity waters derived from most lakes, rivers, and springs.

Rock-salt forms very considerable deposits in many regions; country the most important is situated at Northwich in Cheshire, wh large quantities are extracted by mining. Wielitzka, in Poland, brated for an extensive salt mine, in which there are a chapel an ing-rooms, the furniture of which is made of this rock. Extens of rock-salt also occur in France, Germany, Hungary, Spain, Al and Mexico. Perfectly pure specimens form beautiful colourles and are styled *sal gem;* but ordinary rock-salt is only partially t ent, and exhibits a rusty colour, due to the presence of iron. I places the salt is extracted by boring a hole into the rock an it with water, which is pumped up when saturated with salt, and rated in boilers, the minute crystals of salt being removed as t deposited.

At Droitwich, in Worcestershire, the salt is obtained by evaporat the waters of certain salt springs. In some parts of France and G the water from the salt springs contains so little salt that it wo pay for the fuel necessary to evaporate the water, and a very in plan is adopted, by which the proportion of water is greatly reduc out the application of artificial heat. For this purpose a lofty scaff erected and filled with bundles of brushwood, over which the sa is allowed to flow, having been raised to the top of the scaffol pumps. In trickling over the brushwood this water exposes a l face to the action of the wind, and a considerable evaporation tak so that a much stronger brine is collected in the reservoir ben scaffolding; by several repetitions of the operation, the proportion is so far diminished that the rest may be economically evaporated ficial heat. The brine is run into boilers and rapidly boiled f thirty hours, fresh brine being allowed to flow in continually, maintain the liquid at the same level in the boiler. During this e a considerable deposit, composed of the sulphates of lime and formed, and raked out by the workmen. When a film of crystal begins to form upon the surface, the fire is lowered and the tempe the brine allowed to fall to about 180° F., at which temperat maintained for several days whilst the salt is crystallising. The are afterwards drained and dried by exposure to air. The grai salt is regulated by the temperature at which it crystallises, the si crystals increasing as the temperature falls. It is not possible to the whole of the salt in this way, since the last portions which cr will always be contaminated with other salts present in the brine

quor is not wasted, for after as much salt as possible has been it is made to yield sulphate of soda (Glauber's salt), sulphate of (Epsom salts), bromine and iodine.

rocess adopted for extracting the salt from sea-water depends climate. In Russia, shallow pits are dug upon the shore, in e sea-water is allowed to freeze, when a great portion of the arates in the form of pure ice, leaving a solution of salt suffi- rong to pay for evaporation.

the climate is sufficiently warm, the sea-water is allowed to run ly through a series of shallow pits upon the shore, where it be- ıcentrated by spontaneous evaporation, and is afterwards allowed for some time in reservoirs in which the salt is deposited. The rstals thus obtained are known in commerce as *bay-salt*. Before sent into the market they are allowed to drain for a long time, ered situation, when the chloride of magnesium with which they minated deliquesces in the moisture of the air and drains off. *rn* or liquor remaining after the salt has been extracted is em- furnish magnesia and bromine.

provements have been made during the last few years in the economical of the salts from sea-water. It will be remembered that 1000 parts of contain about

29·0	parts	of chloride of sodium,
0·5	,,	chloride of potassium,
3·0	,,	chloride of magnesium,
2·5	,,	sulphate of magnesia,
1·5	,,	sulphate of lime, &c.

rm climate, that of Marseilles, for example, the water is allowed to evapo- aneously until it has a specific gravity of 1·24. During this evaporation about four-fifths of its chloride of sodium. It is then mixed with one s volume of water and artificially cooled to 0° F. (*see* p. 116), when it de- antity of sulphate of soda, resulting from the decomposition of part of the chloride of sodium by the sulphate of magnesia. The mother-liquor is down till its specific gravity is 1·33, a fresh quantity of chloride of ing deposited during the evaporation. When the liquid cools it deposits alt composed of chloride of potassium and chloride of magnesium, from latter may be extracted by washing with a very little water, leaving the potassium fit for the market.

ocess is instructive as illustrating the influence exerted upon the arrange- e various acids and bases in a saline solution by the temperature to which n is exposed, the general rule being that a salt is formed which is in- the liquid at that particular temperature.

eat tendency observed in ordinary table salt to become damp posed to the air is due chiefly to the presence of small quantities de of magnesium and chloride of calcium, for pure chloride of as very much less disposition to attract atmospheric moisture, it is very easily dissolved by water, $2\frac{3}{4}$ parts of this liquid being ssolve one part (by weight) of salt.

history of the useful applications of common salt is nd
e best illustrations of the influence of chemical n
opment of the resou country, and a cap a
uring process not l processes usu re
e, independent of e of chem t
rect and intentio these t
object.

Until the last quarter of the eighteenth century the uses of common salt were limited to culinary and agricultural purposes, and to the glazing of the coarser kinds of earthenware, whilst a substance far more useful in the arts, *carbonate of soda*, was imported chiefly from Spain under the name of *barilla*, which was the ash obtained by burning a marine plant known as the *salsola soda*. But this ash only contained about one-fourth of its weight of carbonate of soda, so that this latter substance was thus imported at a great expense, and the manufactures of soap and glass to which it is indispensable were proportionally fettered.

During the wars of the French Revolution the price of barilla had risen so considerably, that it was deemed advisable by Napoleon to offer a premium for the discovery of a process by which the carbonate of soda could be manufactured at home, and to this circumstance we are indebted for the discovery, by Leblanc, of the process at present in use for the manufacture of carbonate of soda from common salt, a discovery which placed this substance at once among the most important raw materials with which a country could be furnished.

185. *Manufacture of carbonate of soda from common salt.*—The salt is spread upon the hearth of a *reverberatory* furnace (fig. 219),* and mixed

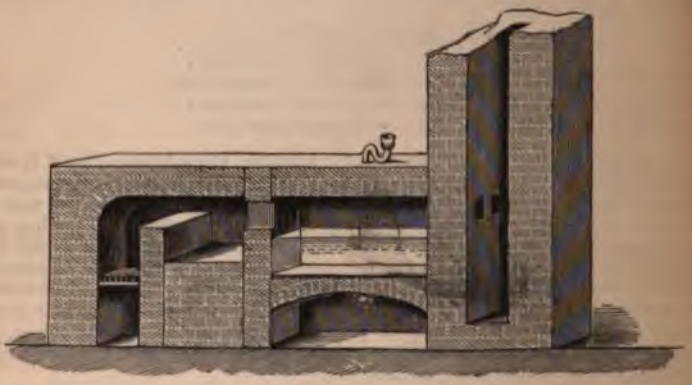


Fig. 219.—Furnace for converting common salt into sulphate of soda.

with an equal weight of sulphuric acid, which converts it into the sulphate of soda (p. 147), expelling the hydrochloric acid in the form of gas, which would prove highly injurious to the vegetation in the neighbourhood, and is therefore usually condensed by being brought into contact with water (*see* p. 148). The flame of the fire is allowed to play over the surface of the mixture of salt and sulphuric acid until it has become perfectly dry; in this state it is technically known as *salt-cake*, and is next mixed with about an equal weight of limestone and rather more than half its weight of small coal; this mixture is again heated upon the hearth of a reverberatory furnace, when it evolves an abundance of carbonic oxide, and yields a mixture of carbonate of soda with

* The hearth of this furnace is usually divided, as seen in the figure, into two compartments, in one of which (lined with lead), more remote from the grate, the decomposition is effected, the acid being poured in through the funnel, while in that nearest to the grate, lined with fire-brick, the whole of the hydrochloric acid is expelled, and the sulphate of soda fused.

ne and sulphide of calcium; this mixture is technically known as *ack ash*.

The change which has been effected in the sulphate of soda will be sily understood; for when this salt is heated in contact with carbon rom the small coal) it loses its oxygen, and becomes sulphide of sodium, hilst carbonic acid is evolved; thus—

$$NaO.SO_3 + C_2 = NaS + 2CO_2 .$$

ain, when carbonate of lime is heated in contact with carbon, carbonic ide is given off, and lime remains—

$$CaO.CO_2 + C = 2CO + CaO .$$

ally, when sulphide of sodium and lime are heated together in the sence of carbonic acid, carbonate of soda and sulphide of calcium are duced—

$$NaS + CaO + CO_2 = NaO.CO_2 + CaS .$$

When the black ash is treated with water, the carbonate of soda is dis-ved, leaving the sulphide of calcium, and by evaporating the solution, linary *soda ash* is obtained. But this is by no means pure carbonate of da, for it contains, in addition to a considerable quantity of common lt and sulphate of soda, a certain amount of caustic soda or hydrate of da formed by the action of the lime upon the carbonate of soda. In der to purify it, the crude soda-ash is mixed with small coal or saw-dust d again heated, when the carbonic acid formed from the carbonaceous mat-r converts the hydrate of soda into carbonate, and on dissolving the mass water and evaporating the solution, it deposits oblique rhombic prisms f common washing soda, having the composition, $NaO.CO_2 + 10Aq.$ *oda-crystals*).

A little reflection will show the important influence which this process as exerted upon the progress of the useful arts in this country. The hree raw materials, salt, coal, and limestone, we possess in abundance. he sulphuric acid, when the process was first introduced, bore a high rice, but the resulting demand for this acid gave rise to so many improve-ents in its manufacture that its price has been very greatly diminished,— circumstance which has, of course, produced a most beneficial effect upon ll branches of manufacture in which the acid is employed.

The large quantity of hydrochloric acid obtained as a secondary product as been employed for the preparation of bleaching powder, and the mportant arts of bleaching and calico-printing have thence received a onsiderable impulse. These arts have also derived a more direct benefit om the increased supply of carbonate of soda, which is so largely used r cleansing all kinds of textile fabrics. The manufactures of soap and lass, which probably create the greatest demand for carbonate of soda, ave been increased and improved beyond all precedent by the production this salt from native sources.

The crystals of carbonate of soda are easily distinguished by their pro-rty of effloresceng in dry air (p. 48), and by their alkaline taste, which is uch milder than that of carbonate of potash, this being, moreover, a eliquescent salt. The crystals are very soluble in water, requiring only 2 rts of cold and less than their own weight of boiling water; the solution strongly alkaline to test papers.

The substance commonly used in medicine under the name of carbona

of soda, is really the *bicarbonate* ($NaO . CO_2 . HO . CO_2$), and is prepared by saturating the carbonate of soda with carbonic acid gas. It is readily distinguished from the carbonate, as it is but slightly alkaline, and is very much less easily dissolved by water.

Soda lye, employed in the manufacture of hard soap, is a solution of *hydrate of soda* ($NaO . HO$), obtained by decomposing the carbonate of soda with hydrate of lime (slaked lime, $CaO . HO$), when the water of this latter compound is exchanged for the carbonic acid of the carbonate.

The solid hydrate of soda of commerce is generally obtained in the process for manufacturing carbonate of soda, just described; the solution obtained by treating the black ash with water is concentrated by evaporation, so that the carbonate and sulphate of soda and chloride of sodium may crystallise out, leaving the hydrate of soda, which is far more soluble, in the liquid. The latter, which still contains a compound of sulphide of sodium and sulphide of iron, which gives it a red colour, is mixed with some nitrate of soda to oxidise the sulphides, and evaporated down until a fused mass of hydrate of soda is left, which is poured out into iron moulds.*

Kryolite ($3NaF . Al_2F_3$) is sometimes employed as a source of the sodium for hydrate of soda, which may be obtained by decomposing it with hydrate of lime.

186. *Sodium.*—Potash and soda exhibit so much similarity in their properties, that we cannot be surprised at their having been confounded together by the earlier chemists, and it was not till 1736 that Du Hamel pointed out the difference between them. The discovery of potassium naturally led Davy to that of sodium, which can be obtained by processes exactly similar to those adopted for procuring potassium, to which it will be remembered sodium presents very great similarity in properties (p. 23). Sodium, however, is readily distinguished from potassium by its burning with a yellow flame, which serves even to characterise it when in combination.

This yellow flame is well seen by dissolving salt in water in a plate, and adding enough spirit of wine to render it inflammable, the mixture being well stirred while burning. If a little piece of sodium be burnt in an iron spoon held in a flame, all the flames in the room, even at a remote distance, will be tinged yellow. The blowpipe flame may also be employed to detect sodium by this colour, as in the case of potassium (p. 261). In fireworks, nitrate of soda is employed for producing yellow flames. A very good *yellow fire* may be made by intimately mixing, in a mortar, 74 grs. of nitrate of soda, 20 grs. of sulphur, 6 grs. of sulphide of antimony, and 2 grs. of charcoal, all carefully dried, and very finely powdered.

The preparation of sodium, by distilling a mixture of carbonate of soda and charcoal, is much easier than that of potassium, for which reason sodium is far less costly than that metal, and has received applications, on the large scale, during the last few years, for the extraction of the metals aluminum and magnesium. An amalgam of sodium (p. 119) is also employed with advantage in extracting gold and silver from their ores.

* Another plan of treating the black ash liquor consists in allowing it to trickle through a column of coke against a current of air, when the sulphide of sodium (NaS) is oxidised and converted into soda (NaO) and hyposulphite of soda ($NaO . S_2O_2$), whilst the sulphide of iron is deposited. The liquor is mixed with a little chloride of lime to oxidise any remaining sulphides, and concentrated by evaporation, when carbonate of soda and ferrocyanide of sodium are deposited in crystals. The liquor separated from these contains the hydrate of soda, and is evaporated till it solidifies on cooling.

o obtain sodium in large quantity, a mixture of dried carbonate of soda, owdered coal, and chalk, is distilled in iron cylinders, when the oxygen the soda is abstracted by the carbon, which it converts into carbonic ide, and the sodium passes over in the form of vapour.

$$NaO.CO_2 + C_2 = Na + 3CO.$$

e chalk is employed to prevent the fusion of the mixture.

187. *Borax*, or *biborate of soda*.—A very important compound of soda used in the arts under the name of *borax*, in which the soda is combined h boracic acid. It has already been stated that this substance is osited during the evaporation of the waters of certain lakes in Thibet, nce it is imported into this country in impure crystals, which are ered with a peculiar greasy coating. The refiner of tincal powders the stals and washes them, upon a strainer, with a weak solution of soda, ich converts the greasy matter into a soap and dissolves it. The borax hen dissolved in water, a quantity of carbonate of soda is added to arate some lime which the borax usually contains, and, after filtering the carbonate of lime, the solution is evaporated to the crystallising nt and allowed to cool, in order that it may deposit the pure crystals borax.

It appears, however, that the greater part of the borax employed in the s is manufactured in this country by heating carbonate of soda with acic acid, when the latter expels the carbonic acid and combines with soda.* The mass is then dissolved in water, and the borax crystal- d, an operation upon which much care is bestowed, since the product s not meet with a ready sale unless in large crystals.

The solution of borax, having been evaporated to the requisite degree of ncentration, is allowed to crystallise in covered wooden boxes, which are ed with lead and enclosed in an outer case of wood, the space between sides of the case and the box being stuffed with some bad conductor heat, so that the solution of borax may cool very slowly, and large stals may be deposited. In about thirty hours the crystallisation is com- ted, when the liquid is drawn off as rapidly as possible, the last portion ng carefully soaked up with sponges, so that no small crystals may be erwards formed upon the surface of the large ones; the case is then in covered up, so that the crystals may cool slowly without cracking.

Borax is chemically known as *biborate of soda*, and is represented, in dry state, by the formula $NaO.2BO_3$. The ordinary prismatic crys- , however, contain ten equivalents of water of crystallisation, and are, refore, represented by the formula $NaO.2BO_3 + 10Aq$. They soon oresce and become opaque when exposed to air, and may readily be inguished by their alkaline taste and action upon test-papers, and ecially by their behaviour when heated, for they fuse easily and *intu- ce* most violently, swelling up to a white spongy mass of many times ir original bulk; this mass afterwards fuses down to a clear liquid ch forms a transparent glassy mass on cooling (*vitrefied borax*), and e this glass is capable of dissolving many metallic oxides with great liness (borax being, by constitution, an acid salt, and therefore ready combine with more base), it is much used in the metallurgic arts. ge quantities of borax are also employed in glazing stoneware.

* The ammonia which is evolved from the Tuscan boracic acid employed in this process own in commerce as *Volcanic ammonia*, and is free from the empyreumatic odour which ally accompanies that from coal and bones.

188. *Silicate of soda.*—A combination of soda with silicic acid has long been used, under the name of *soluble glass*, for imparting a fire-proof character to wood and other materials, and, more recently, for producing artificial stone for building purposes, and for a peculiar kind of permanent fresco-painting (*stereochromy*), the results of which are intended to withstand exposure to the weather.

Soluble glass is usually prepared by fusing 15 parts of sand with 14 parts of carbonate of soda and 1 part of charcoal. The silicic acid, combining with the soda, disengages the carbonic acid, the expulsion of which is facilitated by the presence of charcoal, which converts it into carbonic oxide. The mass thus formed is scarcely affected by cold water, but dissolves when boiled with water, yielding a strongly alkaline liquid.

In using this substance for rendering wood fire-proof, a rather dilute solution is first applied to the wood, and over this a coating of lime-water is laid, a second coating of soluble glass (in a more concentrated solution) is then applied. The wood so prepared is, of course, charred, as usual, by the application of heat, but its inflammability is remarkably diminished.

For the manufacture of *Ransome's artificial stone*, the soluble glass is prepared by heating flints, under pressure, with a strong solution of hydrate of soda, to a temperature between 300° and 400° F., when the silicic acid constituting the flint enters into combination with the soda. The finely divided sand is moistened with this solution, pressed into moulds, dried, and exposed to a high temperature, when the silicate of soda fuses and cements the grains of sand together into a mass of artificial sandstone, to which any required colour may be imparted by mixing metallic oxides with the sand before it is moulded.

Silicate of soda is also sometimes used as a *dung substitute* (p. 240) in calico-printing.

Sulphate of soda forms the very common saline efflorescence upon the surface of brick walls, and has been found covering the sandy soil of the Desert of Atacama, over a considerable area. The mineral known as *Thénardite* also consists of sulphate of soda, and *Glauberite* is a double sulphate of soda and lime ($NaO.SO_3$, $CaO.SO_3$) which is nearly insoluble in water.

Phosphate of soda ($2NaO.HO.PO_5 + 24Aq.$) is obtained by neutralising, with carbonate of soda, the impure phosphoric acid obtained by decomposing bone-ash with sulphuric acid (p. 230). On evaporation the phosphate is deposited in oblique rhombic prisms which effloresce in air.

Nitrate of soda will be more particularly noticed in the section on gunpowder. It is imported from Peru, and used in considerable quantity as a manure, and for the manufacture of nitrate of potash.

Equivalent and atomic weights of sodium.—The analysis of pure chloride of sodium has shown it to contain one equivalent, or 35·5 parts by weight of chlorine combined with 23 parts of sodium; hence 23 is taken to represent the equivalent of sodium. As in the case of potassium, the atomic weight of sodium coincides with the equivalent, the atomic formula of chloride of sodium being NaCl; that of soda would be Na_2O ($O = 16$), and that of hydrate of soda NaHO.

SALTS OF AMMONIA.

ıe great chemical resemblance between some of the salts of ammonia hose of potash and soda has been already pointed out as affording ason for the hypothesis of the existence of a compound metal *onium* (NH_4) equivalent in its functions to potassium and sodium. ever convenient this assumption may be for the purpose of repre- ng by equations the chemical changes in which the salts of ammonia part, it is evidently necessary to place these salts on a different ng from those of potash and soda, until either the metal itself or xide (NH_4O), which is at present equally hypothetical, shall be ned. This has become the more necessary since modern chemistry rought to light certain organic bases which exhibit a stronger resem- ce to potash and soda than that evinced by ammonia, rendering it sary to extend to these also the hypothesis of the existence of com- d metals, and thus to encumber chemical pages with the names of a large of substances of the existence of which there is no direct evidence. uch encouragement has been afforded to the belief in the existence of e of ammonium (NH_4O), by the circumstance that the compounds which formed when ammonia (NH_3) combines with the anhydrous acids, as carbonic (CO_2) and sulphuric (SO_3), do not exhibit the resem- ce to the salts of potash and soda until water is added, the elements hich are required to convert the NH_3 into NH_4O. Thus, by the n of dry ammonia gas upon anhydrous sulphuric acid, a compound d *sulphuric ammonide* is formed, having the composition $NH_3 . SO_3$. substance dissolves in water and crystallises in octahedra, but its ion is not precipitated by chloride of barium, which always precipi- the true sulphates, nor by chloride of platinum which precipitates true salts of ammonia. By long boiling with water, however, it mes converted into the sulphate of ammonia, $NH_3 . HO . SO_3$ (or sul- e of oxide of ammonium, $NH_4O . SO_3$), which yields precipitates with the above tests. The anhydrous phosphoric, carbonic, and sulphurous also combine with dry ammonia to form ammonides, which do not nd to the ordinary tests for the corresponding salts of ammonia until water has been assimilated. The true salts of ammonia are pro- d either by the combination of a hydrated acid with ammonia, or by le decomposition.

lphate of ammonia ($NH_3 . HO . SO_3$) is largely employed in the pre- ion of ammonia-alum, and of artificial manures, for which purposes it nerally obtained from the ammoniacal liquor of the gas-works by ralising with sulphuric acid and evaporating. The rough crystals are y heated to expel tarry substances, and purified by recrystallisation. crystals have the same shape as those of sulphate of potash, and are r soluble in water. When heated to about 500° F. the sulphate mmonia is decomposed, yielding vapour of sulphite of ammonia $_3 . HO . SO_2$), water, ammonia, nitrogen, and sulphurous acid. If in be dipped into a solution of sulphate of ammonia in ten parts of r, and dried, it will no longer burn with flame when ignited. The ral *mascagnine* consists of sulphate of ammonia. This salt is occa- lly found in needle-like crystals upon the windows of rooms in which gas is burnt. The *bisulphate of ammonia* contains $NH_3 . 2(HO . SO_3)$. *equicarbonate of ammonia*, $2NH_3 . 2HO . 3CO_2$ (or $2NH_4O . 3CO_3$), is

the common carbonate of ammonia of the shops, also called *smelling salts* or *Preston salts*, largely used in medicine, and by bakers and confectioners, for imparting lightness or porosity to cakes, &c. It is commonly prepared by mixing sal-ammoniac (hydrochlorate of ammonia) with twice its weight of chalk, and distilling the mixture in an earthen or iron retort communicating, through an iron pipe, with a leaden chamber or receiver, in which the sesquicarbonate of ammonia collects as a transparent fibrous mass, which is extracted by taking the receiver to pieces, and purified by re-subliming it at about 130° F., in iron vessels surmounted by leaden domes. The action of carbonate of lime upon hydrochlorate of ammonia would be expected to furnish the neutral carbonate ($NH_3 . HO . CO_2$), but this salt (even if produced) is decomposed by the heat employed in the process, with loss of ammonia and water, and formation of sesquicarbonate of ammonia—

$$3(NH_3 . HCl) + 3(CaO . CO_2) =$$
$$2NH_3 . 2HO . 3CO_2 + NH_3 + HO + 3CaCl .$$

When a mass of freshly prepared sesquicarbonate of ammonia is exposed to air, it evolves ammonia and carbonic acid, and becomes gradually converted into an opaque crumbly mass of bicarbonate of ammonia—

$$2NH_3 . 2HO . 3CO_2 = NH_3 + CO_2 + NH_3 . 2HO . 2CO_2 .$$

Water effects this decomposition more rapidly; if the powdered sesquicarbonate of ammonia be washed with a little water, bicarbonate of ammonia is left, and the solution contains the elements of neutral carbonate of ammonia ($NH_3 . HO . CO_2$), but this salt has not been obtained in the solid form. The sesquicarbonate dissolves in about three times its weight of cold water. Boiling water decomposes it, and the solution, on cooling, deposits large prismatic crystals of *bicarbonate of ammonia* ($NH_3 . 2HO . 2CO_2$) which is much less soluble in water. This salt has been found in considerable quantity, forming crystalline masses in a bed of guano on the western coast of Patagonia. *Sal volatile* is an alcoholic solution of carbonate of ammonia obtained by distilling sal-ammoniac with carbonate of potash and rectified spirit of wine, or by treating the sesquicarbonate of ammonia with hot spirit.

By dissolving sesquicarbonate of ammonia in strong solution of ammonia, and adding alcohol, prismatic crystals of the sesquicarbonate, of the formula $2NH_3 . 2HO . 3CO_2 + 2Aq.$, may be obtained.

Hydrochlorate of ammonia ($NH_3 . HCl$), or *chloride of ammonium* (NH_4Cl), also called *muriate of ammonia* and *sal-ammoniac*.—When dry ammonia gas is brought in contact with an equal volume of dry hydrochloric acid gas, it has been seen (p. 119) that they combine directly to produce the hydrochlorate of ammonia, the preparation of which on the large scale has been noticed at p. 113. It is also sometimes made by subliming a mixture of sulphate of ammonia with common salt—

$$NH_3 . HO . SO_3 + NaCl = NH_3 . HCl + NaO . SO_3 .$$

Its commercial form is that of a very tough translucent fibrous mass, generally of the dome-like shape of the receivers, and often striped with brown, from the presence of a little iron. It has not the least smell of ammonia, and is very soluble in water, requiring about three parts of cold water, and little more than its own weight of boiling water. As the hot solution cools, it deposits beautiful fern-like crystallisations composed of minute cubes and octahedra. The liquefaction of sal-ammoniac in water

lowers the temperature very considerably, which renders the salt very useful in freezing mixtures. A mixture of equal weights of sal-ammoniac and nitre, dissolved in its own weight of water, lowers the temperature of the latter from 50° F. to 10°. In this case partial decomposition takes place, resulting in the production of chloride of potassium and nitrate of ammonia, both of which absorb much heat whilst being dissolved by water. The solution of hydrochlorate of ammonia in water is slightly acid to blue litmus paper. When sal-ammoniac is heated, it passes off in vapour, at a temperature below redness, without previously fusing; the vapour forms thick white clouds in the air, and may be recondensed as a white crust upon a cold surface; but it cannot be sublimed without some loss, a portion being decomposed into hydrochloric acid, hydrogen, and nitrogen.

The specific gravity (weight of 1 vol.) of the vapour of sal-ammoniac is 0·89. The formula $NH_3.HCl$ represents a compound of 1 eq. or 4 vols. of ammonia (O = 1 vol.), and 1 eq. or 4 vols. of hydrochloric acid.

		sp. gr.		
Weight of 4 vols. of NH_3		(0·59	× 4)	= 2·36
„	4 vols. of HCl	(1·25	× 4)	= 5·00
				7·36

This number obviously represents the weight of 8 vols. of hydrochlorate of ammonia vapour, or one equivalent of this vapour occupies eight times the volume of an equivalent (8 parts by weight) of oxygen, or four times that of an equivalent (1 part by weight) of hydrogen. On the atomic system, according to which one atom of an element occupies one volume, and one molecule of a compound occupies two volumes, hydrochlorate of ammonia vapour should occupy twice the volume of one part by weight of hydrogen, whereas its specific gravity shows it to occupy four times that volume. This anomaly might be explained by supposing a temporary *dissociation* of the hydrochloric acid and ammonia when the salt is converted into vapour, so that the observed specific gravity is really that of a mixture of equal volumes of these constituent gases. Some experimental evidence has been obtained in support of this view, for it has been found that free ammonia and hydrochloric acid may be separated by diffusion from the vapour obtained on heating hydrochlorate of ammonia. When this salt is heated with metallic oxides, its hydrochloric acid often converts the oxide into a chloride which is either fusible or volatile, so that sal-ammoniac is often employed for cleansing the surfaces of metals previously to soldering them. Even those metallic oxides which are destitute of basic properties, such as antimonic and stannic acids, are convertible into chlorides by the action of sal-ammoniac at a high temperature.

Hydrochlorate of ammonia is found in volcanic districts, and is present in very small quantity in sea-water.

Hydrosulphate of ammonia ($NH_3.HS$), or *sulphide of ammonium* (NH_4S), has been obtained in colourless crystals by mixing hydrosulphuric acid gas with twice its volume of ammonia gas in a vessel cooled by a mixture of ice and salt. It is a very unstable compound, decomposing at the ordinary temperature of the air into free ammonia and *bi-hydrosulphate of ammonia*, $NH_3.2HS$, which may be obtained in very volatile colourless needles by passing equal volumes of its constituent gases into a vessel cooled in ice. When a solution of ammonia is saturated with hydrosul-

phuric acid gas, the ammonia is found to have combined with equivalents of hydrosulphuric acid, forming a solution of the bi-hydro phate or *hydrosulphate of sulphide of ammonium* ($NH_4S.HS$). solution is colourless when freshly prepared, but it soon becomes yellow contact with the air, from the formation of the *bisulphide of ammo* (NH_4S_2), hyposulphite of ammonia being formed at the same time—

$$2(NH_4S.HS) + O_3 = NH_4S_2 + NH_4O.S_2O_2 + 2H0.$$

Eventually, the solution deposits sulphur and becomes colourless, hy sulphite, sulphite, and sulphate of ammonia being formed. When freshly prepared colourless solution of the bi-hydrosulphate of ammoni mixed with an acid, the solution remains clear, hydrosulphuric acid b evolved with effervescence; $NH_3.2HS + HCl = NH_3.HCl + 2H$ but if the solution be yellow, a milky precipitate of sulphur is produ from the decomposition of the bisulphide of ammonium—

$$NH_4S_2 + HCl = NH_4Cl + HS + S.$$

The fresh solution gives a black precipitate of sulphide of lead w solution of acetate of lead is added to it, but after it has been kept t is of a dark yellow or red colour, it gives a red precipitate of the sulphide of lead. Solution of hydrosulphate of ammonia, prepared mixing the bi-hydrosulphate with an equal volume of solution of ammo is largely employed in analytical chemistry. The solution has a disagreeable odour.

Bisulphide of ammonium is obtained in deliquescent yellow crystals, when a mi of ammonia gas with vapour of sulphur is passed through a red-hot porcelain It is the chief constituent of *Boyle's fuming liquor*, a fetid yellow liquid obtain distilling sal-ammoniac with sulphur and lime. The bisulphide of ammoniu sometimes deposited in yellow crystals from this liquid. By dissolving sulph the bisulphide of ammonium, orange-yellow prismatic crystals of *pentasulphi ammonium* (NH_4S_5) may be obtained. Even a *heptasulphide of ammonium* (N has been crystallised.

Compounds may be obtained in which the sulphide of ammonium (NH_4S) the part of a sulphur-base towards the sulphides of arsenic, antimony, and sulphur-acids.

It is scarcely possible to represent the constitution of the higher sulphid ammonium except on the ammonium hypothesis.

The *hydrobromate of ammonia* ($NH_3.HBr$), or *bromide of ammonium* (NH_4Br) the hydriodate of ammonia ($NH_3.HI$), or *iodide of ammonium* (NH_4I), are use photography. They are both colourless crystalline salts, but the iodide is very to become yellow or brown, from the separation of iodine, unless kept dry a the dark. Both salts are extremely soluble in water.

LITHIUM is a comparatively rare metal, obtained chiefly from the minerals *l lite* (λεπίς, *a scale*) or *lithia-mica*, containing silicate of alumina with fluori potassium and lithium; *petalite* (πέταλον, *a leaf*), silicate of soda, lithia, and alu and *triphane* or *spodumene* (σποδός, *ashes*), which has a similar composition. Its (from λίθος, *a stone*) was bestowed in the belief that it existed only in the mi kingdom, but recent investigation has detected it in minute proportion in the of tobacco and other plants.

Metallic lithium is obtained by decomposing fused chloride of lithium by vanic current. It is remarkable as the lightest of the solid elements (sp. gr. It bears a general resemblance to potassium and sodium, but is harder an easily oxidised than those metals. It decomposes water rapidly at the ord temperature, but does not inflame upon it.

The alkali lithia (LO) powerfully corrodes platinum when heated upon it, an differs from potash and soda by forming a sparingly soluble phosphate ($3LO.$ and carbonate ($LO.CO_2$). The compounds of lithium impart a red colour flame of the blowpipe (p. 261).

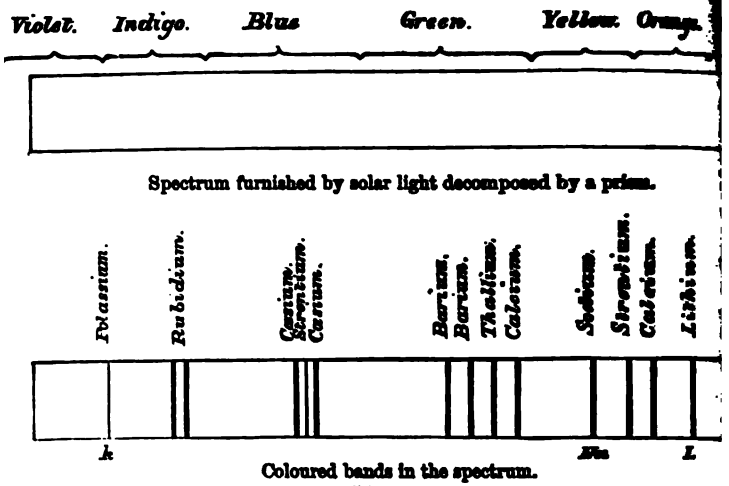
Carbonate of lithia is occasionally employed medicinally.

Rubidium and Cæsium were discovered so lately as in 1860, by Bunsen and Kirchhoff, during the analysis of a certain spring water which contained these metals in so minute quantity (2 or 3 grs. in a ton) that they would certainly have escaped observation if the analysis had been conducted in the ordinary way. The discovery of these metals, as well as of two others (thallium and indium) to be mentioned hereafter, was the result of the application of the method of *spectrum analysis*, of which a brief description is here given, although the discussion of the physical principles upon which it depends would be misplaced in a chemical work.

89. *Spectrum analysis.*—It has been mentioned above that compounds of potassium, sodium, and lithium impart, respectively, lilac, yellow, and crimson colours to the blowpipe flame (or air-gas flame, *see* p. 96), or, in other words, that the highly heated vapours of the metals evolve luminous rays of these particular colours. When the quantity of the metal is extremely minute, and its peculiar luminous rays proportionally scanty, their colour may very easily escape notice, especially if two or three metals are present in the flame at the same time. But if the light emanating from the flame be collected by a lens (at A, fig. 220), and transmitted through a prism of flint glass, or through a hollow prism filled with bisulphide of carbon (B), all the rays of one colour will be refracted in a definite direction, so that the *spectrum*, or image of the flame, when thrown upon a screen, instead of exhibiting colours uniformly distributed like the flame itself, will show stripes or bands of the various coloured rays existing in the flame. Thus, when vapour of sodium is present in the flame, the whole of the yellow light emitted by it will be collected in the *spectrum* into a narrow yellow stripe of great intensity, and so extremely delicate is this test that it is scarcely possible to obtain a flame which does not exhibit this *sodium line*. The heated vapour of lithium emits a mixture of red with a few yellow rays, and accordingly, the spectrum of a flame containing lithium exhibits a very bright band of red light, and a comparatively dull band of yellow light, the red band being characteristic of lithium. The potassium flame emits a mixture of blue and red rays, so that its spectrum exhibits a distinct red band of a darker colour than the lithium band, and a feeble violet band. Instead of throwing the spectrum upon a screen, it is generally passed through a telescope (C) to the eye of the observer, and the *spectroscope* so constructed has now taken its place among the apparatus indispensable to the analytical chemist. The prism B may be slowly moved round by a handle attached to the stage on which it rests, in order that the different parts of the spectrum may be successively brought into sight. By comparing the spectra of the flames containing vapours of the metals with a picture or map of the solar spectrum (fig. 221), the exact position of the various coloured bands may be noted, and thus, if several metals are present in the same flame, they may still be distinguished by the colours and positions of their bands. Thus, if a mixture of the chlorides of potassium, sodium, and lithium be taken upon a loop of *platinum wire and held in the flame*, the dull red line of potassium

Fig. 220.—Spectroscope.

(K, fig. 221) is seen close to one end of the spectrum, at some d
from it the bright red band (L) of lithium; at about the same d



Spectrum furnished by solar light decomposed by a prism.

Coloured bands in the spectrum.

Fig. 221.

from this, the pale yellow lithium line; and close to this, the bright
low band of sodium (Na); whilst near to the other end of the spec
is the feeble violet band of potassium (*k*). The chlorides of the m
are most suitable for this experiment, on account of their easy conv
into vapour.

When examining, with the spectroscope, the alkaline chlorides extracted fr
spring water above alluded to, Bunsen and Kirchhoff observed two red and tw
bands in the spectrum, which they could not ascribe to any known substanc
which they ultimately traced to the two new metals, rubidium (*rubidus*, dar
and cæsium (*cæsius*, *sky-blue*).

Rubidium has since been found in small quantity in other mineral wat
lepidolite, and in the ashes of many plants. This metal is closely related, i
perties, to potassium, but is more easily fusible and convertible into vapou
actually surpasses that metal in its attraction for oxygen, rubidium takin
spontaneously in air. It burns on water with exactly the same flame as pota
Its oxide, *rubidia* (RbO), is a powerful alkali, like potash, and its salts are is
phous with those of potash. The double chloride of platinum and potassium,
ever, is eight times as soluble in boiling water as the corresponding salt of rubi
which is taken advantage of in separating these two allied metals.

Cæsium appears to be even more highly electropositive than rubidium, form
strong alkali, cæsia (CsO), with oxygen, and salts which are isomorphous with
of potassium. Carbonate of cæsia, however, is soluble in alcohol, which do
dissolve the carbonates of potash and rubidia. Moreover, the bitartrate of ca
is nine times as soluble in water as the bitartrate of rubidium.

Cæsium has been found in lepidolite; and the rare mineral *pollux*, found in
and resembling feldspar in composition, is said to contain a very large quan
this metal.

190. *General review of the group of alkali-metals.*—Cæsium, rubi
potassium, sodium, and lithium, constitute a group of elements conspi
for their highly electropositive character, the powerfully alkaline nat
their oxides, and the general solubility of their salts. Their chemica
racters and functions are directly opposite to those of the electrone
group containing fluorine, chlorine, bromine, and iodine, and, like tho

ts, they exhibit a gradation of properties. Thus, cœsium appears to be most highly electropositive member, rubidium the next, then potassium sodium, whilst lithium is the least electropositive; and just as iodine, least electronegative of the halogens, possesses the highest equivalent mber, so cœsium, the least electronegative (or most electropositive) of alkali-metals, has a higher equivalent than any other member of this up, their equivalent weights being represented by the numbers, sium, 133: rubidium, 85·3; potassium, 39; sodium, 23; lithium, 7. in the case of the halogens, also, there is no reason to believe that the mic weights of this group differ from their equivalent weights, so that y are all uni-equivalent elements. Just as chlorine is accepted as the presentative of *chlorous radicals*, so potassium is commonly regarded as type of *basylous radicals*, the term radical being applied to all subnces, whether elementary or compound, which are capable of being nsferred, like chlorine or potassium, from one compound to another thout suffering decomposition.

Some of the physical properties of these elements exhibit a gradation the same order as their equivalent weights; thus rubidium fuses at 1° F., potassium at 144°·5, sodium at 207°·7, and lithium at 356°, so at, at ordinary temperatures, rubidium is the softest, and lithium the rdest of these metals.

In some of their salts a similar gradational relation is observed; the rbonates, for example, of cœsia, rubidia, and potassa, are highly deliquescent, absorbing water greedily from the air, whilst carbonate of soda not deliquescent, and carbonate of lithia is sparingly soluble in water. he difficult solubility of the carbonate and phosphate of lithia constiutes the connecting link between this and the succeeding group of metals, he carbonates and phosphates of which are insoluble in water.

BARIUM.

191. Barium, so named from the great weight of its compounds (*βαρύς, heavy*) is found in considerable abundance in the north of England, in two minerals known as *Witherite* (carbonate of baryta, $BaO.CO_2$) and *heavy spar* (sulphate of baryta, $BaO.SO_3$). Witherite is found in large masses in the lead mines at Alston Moor, and at Anglesark in Lancashire. It is said to be used for poisoning rats, and was originally mistaken, on account of its great weight, for an ore of lead.

The metal itself is obtained by decomposing fused chloride of barium by the galvanic current. It is a pale yellow, fusible, malleable metal of sp. gr. about 4, which is easily oxidised by air, and rapidly decomposes water at common temperatures.

Such compounds of baryta as are used in the arts are chiefly prepared from heavy spar or sulphate of baryta, which is remarkable for its insolubility in water and acids. In order to prepare other compounds of baryta from this refractory mineral, it is ground to powder and strongly heated in contact with charcoal or some other carbonaceous substance, which removes the oxygen from the mineral in the form of carbonic oxide, and converts it into *sulphide of barium*; $BaO.SO_3 + C_4 = 4CO + BaS$. This latter compound, being soluble in water, can be readily converted into other barytic compounds.

The artificial *sulphate of baryta* which is used by painters, instead of *white lead, under the name of permanent white*, and is employed for

glazing cards, is prepared by mixing the solution of sulphide of b with dilute sulphuric acid, when the sulphate of baryta separat white precipitate, which is collected, washed, and dried—

$$BaS + HO.SO_3 = HS + BaO.SO_3.$$

The artificial *carbonate of baryta*, which is used in the manufac some kinds of glass, is prepared by passing carbonic acid gas thr solution of sulphide of barium, when the carbonate of baryta is p tated; $BaS + HO + CO_2 = HS + BaO.CO_2$.

In preparing compounds of barium from heavy spar on the small sc better to convert the sulphate of baryta into carbonate of baryta. 50 gr. finely powdered sulphate are mixed with 100 grs. of dried carbonate of so grs. of powdered nitre, and 100 grs. of very finely powdered charcoal. The is placed in a heap upon a brick or iron plate, and kindled with a match, wh heat evolved by the combustion of the charcoal in the oxygen of the nitre, fu sulphate of baryta with the carbonate of soda, when they are decomposed in bonate of baryta and sulphate of soda—

$$BaO.SO_3 + NaO.CO_2 = NaO.SO_3 + BaO.CO_2.$$

The fused mass is thrown into boiling water, which dissolves the sulphate and leaves the carbonate of baryta. The latter may be allowed to sett washed several times, by decantation, with distilled water, until the washi longer yield a precipitate with chloride of barium, showing that the whole sulphate of soda has been washed away, and pure carbonate of baryta remai

Nitrate of baryta ($BaO.NO_5$) is obtained by dissolving carbon baryta in diluted nitric acid, and evaporating the solution, when hedral crystals of the nitrate are deposited. It is an ingredient in kinds of blasting powder used by miners. If nitrate of baryta be in a porcelain crucible, it fuses and is decomposed, leaving a grey mass of *baryta*; $BaO.NO_5 = BaO + NO_4 + O$.

Hydrate of baryta may be procured by adding 4 oz. of the po nitrate of baryta to 12 oz. of a boiling solution of hydrate of soda, gr. 1·13 (prepared by dissolving 3 oz. of commercial hydrate of s 20 measured ounces of water); the solution becomes turbid fro separation of carbonate of baryta produced from the carbonate of s the hydrate; it is boiled for some minutes and then filtered; on cooling, some crystals of undecomposed nitrate of baryta are dep and if the clear liquid be poured off into another vessel and sti deposits abundant crystals of hydrate of baryta, having the comp $BaO.HO + 8Aq.$; these effloresce and become opaque when exp air, becoming $BaO.HO + Aq.$; when heated to redness, they l pure hydrate of baryta, BaO.HO, which fuses, but is not decor when further heated. The hydrate of baryta is moderately solu water, the solution being strongly alkaline, and absorbing carbon from the air, depositing carbonate of baryta.

When baryta is heated in a tube through which oxygen or air is it absorbs the oxygen and is converted into binoxide of barium (which is employed for the preparation of binoxide of hydrogen (*see*

Chloride of barium, which is the barium compound most com employed in the laboratory, may be obtained by dissolving the car of baryta in diluted hydrochloric acid, and evaporating the solutio cooling, the chloride is deposited in tabular crystals, $BaCl + 2Aq.$

On the large scale it is generally manufactured by fusing heav (sulphate of baryta) with chloride of calcium (the residue from th uration of ammonia, *see* p. 114), in a reverberatory furnace—

$$BaO.SO_3 + CaCl = CaO.SO_3 + BaCl.$$

mass is rapidly extracted with hot water, which leaves the sulphate me undissolved, and the clear solution of chloride of barium is de-d and evaporated. If the sulphate of lime and chloride of barium allowed to remain long together in contact with the water, sulphate aryta and chloride of calcium would be reproduced.

hlorate of baryta ($BaO . ClO_5$) is employed in the manufacture of fire-ks, being prepared for that purpose by dissolving the artificial car-ate of baryta in solution of chloric acid; it forms beautiful shining lar crystals. When mixed with combustible substances, such as coal and sulphur, it imparts a brilliant green colour to the flame of burning mixture (*see* p. 158).

ll the soluble salts of barium are very poisonous.

STRONTIUM.

192. Strontium is less abundant than barium, and occurs in nature in ilar forms of combination. *Strontianite*, the *carbonate of strontia* ($SrO . CO_2$), was first discovered in the lead mines of Strontian in Argyle-re, and has since been found in small quantity in some mineral waters. *Celestine* (so called from the blue tint of many specimens) is the *sul-ate of strontia* ($SrO . SO_3$), and is found in beautiful crystals associated h the native sulphur in Sicily. It is also met with in this country, l is the source from which the *nitrate of strontia* employed in firework mpositions is derived. The sulphate of strontia resembles that of yta with respect to its insolubility, and is converted into the soluble *phide of strontium* (SrS) by calcination with carbonaceous matter. e solution of sulphide of strontium so obtained is decomposed by nitric d, and the nitrate of strontia crystallised from the solutions. This salt ms prismatic crystals which have the formula $SrO . NO_5 + 5Aq$. It s the property of imparting a magnificent crimson colour to flames, and hence largely used for the preparation of red theatrical fires. (*See* 158). The other compounds of strontium possess too little practical portance, and too nearly resemble those of barium, to require particular scription here. No peroxide of strontium, however, has been obtained. The metal itself is prepared in a similar manner to metallic barium, ich it much resembles, though it is lighter (sp. gr. 2·54) and less ible. It burns, when heated in air, with a crimson flame.

CALCIUM.

193. No other metal is so largely employed in a state of combination calcium, for its oxide, lime (CaO), occupies among bases much the e position as that which sulphuric acid holds among the acids, and is d, directly or indirectly, in most of the arts and manufactures.

Like barium and strontium, it is found, though far more abundantly n these, in the mineral kingdom, in the forms of carbonate and sul-te, but it also occurs in large quantity as fluoride of calcium (p. 177), l less frequently in the form of phosphate of lime (p. 222). Calcium, reover, is found in all animals and vegetables, and its presence in their d, in one form or other, is an essential condition of their existence.

Metallic calcium may be obtained by decomposing fused iodide of cal-*m with metallic sodium. It has a light golden-yellow colour, is harder*

than lead, and very malleable; it oxidises slowly in air at the or temperature, but when heated to redness, it fuses and burns with brilliant white light, being converted into lime (*calx*). It deco water at the ordinary temperature. It is lighter than barium and tium, its specific gravity being 1·58.

Carbonate of Lime, from which all the manufactured compo lime are derived, constitutes the different varieties of limestone wh met with in such abundance.

Limestones and *chalk* are simply carbonate of lime in an amorp uncrystallised state. The *oolite* limestone, of which the Bath an land building-stones are composed, is so called from its resemblance roe of a fish (ωον, an egg.) *Marble*, in its different varieties, is an blage of minute crystalline grains of carbonate of lime, sometime gated by the presence of oxides of iron and manganese, or of bitu matter. This last constituent gives the colour to black marble. bonate of lime is also found in large transparent rhombohedral c which are known to mineralogists as *calcareous spar*, *calc spar*, or *spar*. When the crystals have the form of a six-sided prism, the is termed *Arragonite*. The attention of the crystallographer h been directed to these two crystalline forms of carbonate of lime, count of the circumstance, that if a prism of arragonite be heated, it up into a number of minute rhombohedra of calc spar.

Carbonate of lime is a chief constituent of the shells of fishes egg shells, so that, except phosphate of lime, no mineral compou so large a share in the composition of animal frames. *Corals* al sist chiefly of carbonate of lime derived from the skeletons of in able minute insects. The mineral *gaylussite* is a double carbo lime and soda ($CaO.CO_2$, $NaO.CO_2$ + 5Aq.), and is scarcely by water unless previously heated, when water dissolves out t bonate of soda. *Baryto-calcite* is a double carbonate of baryta a ($BaO.CO_2$, $CaO.CO_2$).

Lime.—The process by which lime is obtained from the carbo been already alluded to under the name of lime-burning. In ord the carbonic acid may be completely expelled from the carbonate it is necessary that the products of combustion of the fuel sh allowed to pass over the limestone, since although a very inten is insufficient to decompose carbonate of lime when shut up in a c the decomposition is easily effected if the carbonate be heated i rent of atmospheric air or of any other gas, especially if aqueous be present, as is the case in the products of combustion of the fuel

Accordingly, a kiln is commonly employed of the form of an i cone of brickwork (fig. 222), and into this the limestone and thrown in alternate layers. The former losing its carbonic acid it reaches the bottom of the furnace, is raked out in the form or *quick* lime (CaO), whilst its place is supplied by a fresh layer stone thrown in at the top of the kiln. Fig. 223 represents anot of kiln, in which the limestone is supported upon an arch bu large lumps of the stone above the fire, which is kept burning f three days and nights, until the whole of the limestone is decomp

The usual test of the quality of the lime thus obtained co sprinkling it with water, with which it should eagerly combin ing much heat, swelling greatly, and crumbling to a light white of *hydrate of lime* (*slaked lime*). Lime which behaves in this w

ed *fat lime*; whereas, if it be found to slake feebly, it is pronounced *or lime*, and is known to contain considerable quantities of foreign tances, such as silica, alumina, magnesia, &c. Lime is said to be *burnt* when it contains hard cinder-like masses of silicate of lime,

Fig. 222.—Lime-kiln.

Fig. 223.—Lime-kiln.

ned by the combination of the silica, which is generally found in lime-ne, with a portion of the lime, under the influence of excessive heat in kiln.

he hydrate of lime is about twice as soluble in cold as it is in hot er, so that *lime-water* should always be made by shaking slaked with cold distilled water, which dissolves about 1-700th of its weight; solution is allowed to settle in a closed bottle, for it absorbs carbonic rapidly from the air. Crystals of hydrate of lime have been obtained vaporating lime-water *in vacuo*.

ULPHATE OF LIME in combination with water ($CaO . SO_3 . HO + Aq.$) et with in nature, both in the form of transparent prisms of *selenite*, in opaque and semi-opaque masses known as *alabaster* and *gypsum*. s this latter form which yields *plaster of Paris*, for when heated to ween 300° and 400° F., it loses its water, and if the mass be then dered, and again mixed with water, the powder recombines with it rm a mass of hydrated sulphate of lime, the hardness of which nearly ls that of the original gypsum.

the preparation of plaster of Paris, a number of large lumps of um are built up into a series of arches, upon which the rest of the um is supported; under these arches the fuel is burnt, and its flame lowed to traverse the gypsum, care being taken that the temperature not rise too high, or the gypsum is *over-burnt* and does not exhibit property of recombining with water. When the operation is supposed e completed, the lumps are carefully sorted, and those which appear ve been properly calcined are ground to a very fine powder. When powder is mixed with water to a cream, and poured into a mould, the te particles of anhydrous sulphate of lime ($CaO . SO_3$) combine with s. of water to reproduce the original gypsum ($CaO . SO_3 . HO + Aq.$), this act of combination is attended with a slight expansion which s *the plaster into the finest lines* of the mould.

Stucco consists of plaster of Paris (occasionally coloured) mixed with a solution of size; certain cements used for building purposes (Keene's and Keating's cements) are prepared from burnt gypsum, which has been soaked in a solution of alum and again burnt; and although the plaster thus obtained takes much longer to set than the ordinary kind, it is much harder, and therefore takes a good polish.

Plaster of Paris is much damaged by long exposure to moist air, from which it regains a portion of its water, and its property of setting is so diminished.

Precipitated sulphate of lime is used by paper-makers under the name of *pearl hardener*.

Chloride of calcium has been mentioned as the residue left in the preparation of ammonia. The pure salt may be obtained by dissolving pure carbonate of lime (white marble) in hydrochloric acid, and evaporating the solution, when prismatic crystals of the composition CaCl + 6Aq are obtained. When these are heated they melt, and at about 390° F. are converted into a white porous mass of CaCl + 2Aq., which is much used for drying gases. At a higher temperature, fused chloride of calcium free from water, is left; this is very useful for removing water from some liquids.

When hydrate of lime is boiled with a strong solution of chloride of calcium, it is dissolved, and the filtered solution deposits prismatic crystals of *oxychloride of calcium*, CaCl.3CaO + 15Aq., which are decomposed by pure water.

Less important compounds of calcium not previously noticed.

Sulphide of calcium,	CaS	Pentasulphide of calcium,	CaS_5
Bisulphide „	CaS_2	Silicide „	$CaSi_2$

MAGNESIUM.

194. Magnesium is found, like calcium, though less abundantly, in each of the three natural kingdoms. Among minerals containing the metal, those with which we are most familiar are certain combinations of silica and magnesia (silicates of magnesia) known by the names of *talc*, *steatite* or *French chalk*, *asbestos*, and *meerschaum*, which always contain water. *Magnesite* is a carbonate of magnesia. Most of the minerals containing magnesium have a remarkably soapy feel. The compounds of magnesium, which are employed in medicine, are derived either from the mineral *dolomite* or *magnesian limestone*, which contains the carbonate of magnesia and carbonate of lime, or from the sulphate of magnesia which is obtained from sea-water and from the waters of many mineral springs.

Metallic magnesium has acquired some importance during the last few years as a source of light. When the extremity of a wire of this metal is heated in a flame, it takes fire, and burns with a dazzling white light, becoming converted into magnesia (MgO). If the burning wire be plunged into a bottle of oxygen, the combustion is still more brilliant. The light emitted by burning magnesium is capable of inducing chemical changes similar to those caused by sun-light, a circumstance turned to advantage for the production of photographic pictures by night. Attempts have been made to introduce magnesium as an illuminating agent for general purposes, but the large quantity of solid magnesia produced in the

bustion forms a very serious obstacle to its use. The metal is extracted from the chloride of magnesium (*see* p. 108) by fusing it with sodium, using chloride of sodium and fluoride of calcium to promote the fusibility of the mass.

On a small scale magnesium may be prepared by mixing 900 grs. of chloride of magnesium with 150 grs. of fluoride of calcium, 150 of fused chloride of sodium, and 150 of sodium cut into slices (*see* p. 108). The mixture is thrown into a red-hot earthen crucible, which is then covered and again heated. When the action appears to have terminated, the fused mass is stirred with an iron rod to promote the union of the globules of magnesium. It is then poured upon an iron tray, allowed to solidify, broken up, and the globules of magnesium separated from the slag; they may be collected into one globule by throwing them into a melted mixture of chlorides of magnesium and sodium and fluoride of calcium.

In most of its physical and chemical characters magnesium resembles zinc, though its colour more nearly approaches that of silver; in ductility and malleability it also surpasses zinc. It is nearly as light, however, as calcium, its specific gravity being 1·74. It fuses below a red heat, and may be distilled like zinc. Cold water has scarcely any action upon magnesium; even when boiled it oxidises the metal very slowly. In the presence of acids, however, it is rapidly oxidised by water. Solution of hydrochlorate of ammonia also dissolves it, owing to the tendency of the magnesium salts to form double salts with those of ammonia—

$$2(NH_3 . HCl) + Mg = NH_3 . HCl, MgCl + H + NH_3 .$$

Magnesium is one of the few elements which unite directly with nitrogen at a high temperature. The *nitride of magnesium*, NMg_3, has been obtained in transparent crystals, and is evidently composed after the type NH_3, so that it is not surprising that the action of water upon it gives rise to magnesia and ammonia, $NMg_3 + 3HO = NH_3 + 3MgO$.

The *sulphate of magnesia*, so well known as Epsom salts, is sometimes prepared by calcining dolomite to expel the carbonic acid, washing the residual mixture of lime and magnesia with water to remove part of the lime, and treating it with sulphuric acid which converts the lime and magnesia into sulphates; and since the sulphate of lime is almost insoluble in water, it is readily separated from the sulphate of magnesia which passes into the solution, and is obtained by evaporation in prismatic crystals having the composition $MgO . SO_3 . HO + 6Aq$. The preparation of Epsom salts from sea-water has already been alluded to (p. 263). In some parts of Spain, sulphate of magnesia is found in large quantities (like nitre in hot climates) as an efflorescence upon the surface of the soil. This sulphate of magnesia, as well as that contained in well-waters, appears to have been produced by the action of sulphate of lime, originally present in the water, upon magnesian limestone rocks; $MgO . CO_2 + CaO . SO_3 = MgO . SO_3 + CaO . CO_2$.

The water of constitution in the sulphate of magnesia may be displaced by the sulphate of an alkali without alteration in its crystalline form; a double sulphate of magnesia and potash ($MgO . SO_3$, $KO . SO_3 + 6Aq.$), and a similar salt of ammonia ($MgO . SO_3$, $NH_3 . HO . SO_3 + 6Aq.$) may be thus obtained. The mineral *polyhalite* (πολὺς, *many*, ἅλς, *salt*) is a remarkable salt, containing $MgO . SO_3$, $KO . SO_3$, $2(CaO . SO_3) + 2HO$. Water decomposes it into its constituent salts.

The preparation commonly used in medicine under the name of *magnesia, is really a basic carbonate of magnesia*, or a compound of carbonate

of magnesia with hydrate of magnesia and water in the proporti expressed by the formula, $3(MgO . CO_2) . MgO . HO . 3Aq$. It is obtain by mixing boiling solutions of sulphate of magnesia and carbonate of so when one-fourth of the carbonic acid is expelled in the state of gas; t white precipitate is thrown upon a cloth strainer, well washed, and dr in rectangular moulds.

Another process for preparing carbonate of magnesia consists in heat magnesian limestone to low redness, so as to decompose the carbonat magnesia which it contains, and exposing it, under pressure, to the act of water and carbonic acid, which dissolves the magnesia and leaves carbonate of lime. On boiling the solution, to expel the excess of bonic acid, the carbonate of magnesia is precipitated.

By moderately heating the carbonate of magnesia, its water and carbo acid are expelled, and pure or *calcined magnesia* (MgO) is left, whic very slightly soluble in water and feebly alkaline.

The mineral *periclase* consists of magnesia in a crystallised fo Magnesia combines with water to form a hydrate (MgO . HO), but with evolution of heat, as in the cases of baryta, strontia, and li Crystallised hydrate of magnesia constitutes the mineral *brucite*. M nesia, like lime, is remarkable for its infusibility.

It has recently been noticed that calcined magnesia, when mixed w water, solidifies after a time into a very hard compact mass of hydrat magnesia (MgO . HO), and may serve, like plaster of Paris, for taking c Dolomite calcined below redness also sets to a very hard mass with w This *hydraulicity* of magnesia is likely to meet with useful applicatio

The *phosphate of magnesia* ($3MgO . PO_5$) enters into the composition bones, and the *phosphate of magnesia and ammonia* ($2MgO . NH_3 . HO . P$ or *triple phosphate*, is found in calculi and in the minerals *guanite struvite*.

Borate of magnesia composes the mineral *boracite; hydroboracite* hydrated borate of lime and magnesia.

Serpentine and *olivine* are silicates of magnesia and protoxide of i Some of the varieties of serpentine are employed for preparing the c pounds of magnesia, for they are easily decomposed by acids with se tion of silica.

Pearl-spar is a crystallised carbonate of lime and magnesia.

Chloride of magnesium is important as the source of metallic m nesium. It is easily obtained in solution by neutralising hydroch acid with magnesia or its carbonate, but if this solution be evaporate order to obtain the dry chloride, a considerable quantity of the s decomposed by the water at the close of the evaporation, leaving a magnesia mixed with the chloride ($MgCl + HO = HCl + MgO$). decomposition may be prevented by mixing the solution with three of hydrochlorate of ammonia for every part of magnesia, when a do salt ($MgCl, NH_3 . HCl$) is formed, which may be evaporated to dry without decomposition, and leaves fused chloride of magnesium v further heated, the hydrochlorate of ammonia being volatilised. chloride of magnesium absorbs moisture very rapidly from the air, a very soluble in water. Like all the soluble salts of magnesium, it h decidedly bitter taste.

195. *General review of the metals of the alkaline earths.*—Ba ontium, calcium, and magnesium form a highly interesting gr

up of metals related to each other in a most remarkable manner. ey exhibit a marked gradation in their attraction for oxygen ; barium is re readily tarnished or oxidised, even in dry air, than strontium, and ontium more readily than calcium ; whilst magnesium is not at all ected by dry air, and is comparatively slowly tarnished even in moist . Again, the three first metals decompose water at the ordinary tempera- re, combining with its oxygen and liberating the hydrogen, but mag- sium requires the aid of heat to effect this decomposition. The oxides the metals exhibit a similar gradation in properties ; baryta, strontia, d lime combine with water very energetically with great evolution of at, whilst in the case of magnesia no rise of temperature is observed ; e hydrate of baryta does not lose its water, however strongly it may be ated, whereas the hydrates of strontia and lime are decomposed at a red at, and hydrate of magnesia even at a lower temperature. Then hydrate baryta and hydrate of strontia are far more soluble in water than hydrate lime (which requires about 700 parts of water to dissolve it), and all ese three exhibit a very decided alkaline reaction which entitles them the name of *alkaline earths*, but hydrate of magnesia requires about 000 parts of water to dissolve it, and is so feebly alkaline, that it might en be fairly classed among the *earths proper*. Among the other com- unds of these metals, the sulphates may be named as presenting a adation of a similar description ; for sulphate of baryta may be said to e insoluble in water, sulphate of strontia dissolves to a very slight extent, lphate of lime is rather more soluble, and the sulphate of magnesia is ry readily dissolved by water.

It will be seen hereafter that the sulphates of the earths proper are markable for their solubility in water, so that, in this respect also, mag- sia appears to stand on the border line between the two classes. The nner in which these metals are associated in nature is also not without significance, for if two of them are found in the same mineral, they ll usually be those which stand next to each other in the group ; thus rbonate of strontia is found together with carbonate of baryta in therite, whilst carbonate of lime is associated with the sulphate of ontia in celestine. Again, carbonate of strontia is often found with rbonate of lime in arragonite, and the carbonate of magnesia occurs with rbonate of lime in dolomite.

196. *Equivalent and atomic weights of barium, strontium, calcium, d magnesium.*—The analysis of chloride of barium has proved it to con- n 68·5 parts by weight of barium, combined with 1 eq. (35·5 parts) of lorine ; whence the equivalent of barium is accepted as 68·5. In a nilar manner, that of strontium has been fixed at 43·8, that of calcium 20, and that of magnesium at 12 ; so that here, as in the group of tali-metals, the equivalent numbers decrease with the diminution of the ctropositive character in the metals.

Relation between specific heats and equivalent weights. Atomic heats.— ace the specific volumes of the vapours of these metals have not been ertained, recourse is had to their specific heats in order to ascertain eir atomic weights. It will be remembered that the specific heat of a bstance is the quantity of heat required to raise it 1° in temperature, as mpared with the quantity of heat required to raise an equal weight of ter 1° ; or, more concisely, the quantity of heat required to raise one t *by weight of the substance* 1° (referred to water as the unit).

Thus, the specific heats of potassium, sodium, and lithium are, respectively, 0·1696, 0·2934, and 0·9408; these numbers representing the relative quantities of heat required to raise one part by weight of each of these metals 1° in temperature, supposing that an equal weight of water would be raised 1° by a quantity of heat expressed by *one*. No simple relation can be traced between these numbers, but if the quantities of heat be calculated which are required to raise *equivalent* weights of these elements 1°, the case will be different.

If 0·1696 be the quantity of heat required to raise one part by weight of potassium 1°, 0·1696 × 39, or 6·61, will represent the quantity of heat required to raise 39 parts (1 eq.) of potassium 1°. In the same way, 0·2934 × 23, or 6·75, is the quantity of heat required to raise 23 parts (1 eq.) of sodium 1°; and 0·9408 × 7, or 6·59, is the quantity required to raise 7 parts (1 eq.) of lithium 1°. Allowing for experimental error in the determination of the specific heats, these numbers, 6·61, 6·75, and 6·59, may be regarded as representing the same quantities of heat. Since the atomic weights of potassium, sodium, and lithium are expressed by the same numbers as their equivalent weights (*see* p. 275), the numbers 6·61, 6·75, and 6·59, would represent the *atomic heats* of these metals, that is, the relative quantities of heat required to raise an atom of each 1° in temperature.

(DEF.—The *atomic heat* of a substance is the number obtained by multiplying its specific heat by its atomic weight.)

The atomic heat, therefore, which is common to these three metals, may be represented by the mean of the three numbers, or 6·65.

The experiments which have been made to determine the specific heats of those elements which can be obtained in a similar physical condition, lend strong support to the belief that the atomic heats of all elements belonging to the same group are identical, and even hold out a prospect of the identity of the atomic heats of a great majority of the elementary bodies. The atomic heats of oxygen, hydrogen, and nitrogen are, respectively, 3·48, 3·41, and 3·41, and may therefore be considered to be identical.

A similar relation has been observed between the atomic heats of compound bodies belonging to the same group; thus, if the specific heats of the chlorides of potassium, sodium, and lithium be multiplied by the atomic weights of those chlorides, the product in each case will approach very nearly to the number 12·69. If these chlorides be allowed to contain one atom of each of their constituents, and it be supposed that the atomic heats of these constituents are identical, the half of this number (or 6·34) should represent the atomic heat of the alkali-metals, and, in fact, it does nearly coincide with that number (6·65).

The specific heats of barium, strontium, and calcium have not been determined, and therefore their atomic heats cannot be directly ascertained. The specific heat of magnesium, however, is 0·2499, and if the atomic weight of this metal were identical with its equivalent (12), its atomic heat would be represented by the number 3; but if the atomic weight be regarded as double the equivalent, or 24, the atomic heat will be (0·2499 × 24) 6, a number more nearly approaching to the atomic heats of the alkali-metals. This is one reason for supposing that the atomic weight of magnesium is really represented by 24 (Mg).

The specific heats of the chlorides of barium, strontium, calcium, and esium have been ascertained to be represented by the numbers 0, 0·1180, 0·1686, and 0·1970, respectively. Now, if the atomic

these metals be regarded as identical with their equivalent
atomic heats of the chlorides, obtained by multiplying their
hts into their specific heats, would be expressed by the mean
5, and if this be divided by 2 (the presumed number of atoms in
le), it would give 4·68 for the atomic heat of each of the ele-
compound, a number which exhibits no simple relation to the
of magnesium, or to those of the alkali-metals. If it be sup-
ever, that the atom of barium, strontium, calcium, or mag-
ly represents two equivalents, so that each chloride contains
ntary atoms (two of chlorine and one of metal), the atomic
ch of the chlorides would be doubled, and, consequently, the
would be twice that given above, or 18·72. Dividing this by
med number of atoms in the chloride, we obtain the number
atomic heat of each of the elements, which agrees very well
irectly obtained for magnesium and the alkali-metals.
ls barium, strontium, calcium, and magnesium, therefore, are
garded as bi-equivalent or diatomic elements, one atom of each
he place of two atoms of hydrogen, their atomic weights being
87·5, Ca 40, Mg 24. The atomic formulæ of their oxides
BaO, SrO, CaO, and MgO, and that of their chlorides $BaCl_2$,
$_2$ and $MgCl_2$.*
omic formulæ were generally adopted, the absence of the
ween the formulæ of the oxides and those of the chlorides
ound to detract from the simplicity of many of the equations
of chemical changes in which these metals are concerned.

ALUMINUM.

minum is the representative of the class of metals usually
ls of the earths proper, and including also glucinum, thorinum,
conium, erbium, terbium, cerium, lanthanum, and didymium,
, aluminum is the only metal having any claim to our attention
nd of its practical importance.
m is distinguished among metals, as silicon is among non-
lies, for its immense abundance in the solid mineral portion of
which, indeed, it is almost entirely confined, for it is present
s and animals in so small quantity that it can scarcely be re-
rming one of their necessary components.
he oldest rocks, which appear to have originally formed the
solid structure of the globe, is that known as *granite*. This
ich derives its name from its conspicuous *granular* structure,
, in variable proportions, of quartz, feldspar, and mica, tinged
colours by the presence of small quantities of the oxides of
nganese.
which forms the translucent or transparent grains in the granite,
ply of silicic acid; *feldspar*, the dull cream-coloured opaque
combination of that acid with alumina and potash, and is
oken of as a double silicate of alumina and potash, its com-
ng represented by the formula $KO . 3SiO_2 . Al_2O_3 . 3SiO_2$.
named from the *glittering* scales which it forms in the granite,
uble silicate of alumina and potash, but the alumina is very
lisplaced by sesquioxide of iron, and the potash by magnesia.

* *argument for the diatomic character* of barium will be found at p. 256.

By the long-continued action of air and water, the granite rock is gradually crumbled down or disintegrated, an effect which must be ascribed to a concurrence of mechanical and chemical causes. Mechanically, the rock is continually worn down by variations of temperature, by the congelation of water within its minute pores, the rock being gradually split by the expansion attendant upon such congelation. Chemically, the action of water containing carbonic acid would tend to remove the potash from the feldspar and mica in the form of carbonate of potash, whilst the silicate of alumina and the quartz would subsequently be separated by the action of water; the former, being so much lighter, would be soon washed away from the heavy quartz, and, when again deposited, would constitute *clay*.

Although clay, therefore, always consists mainly of silicate of alumina, it generally contains some uncombined silicic acid, together with variable quantities of lime, of oxide of iron, &c., which give rise to the numerous varieties of clay.

Composition of Clay.

	Chinese Kaolin.	Fire-clay. (Stourbridge).	Pipe-clay.
Silica . . .	50·5	64·1	53·7
Alumina . .	33·7	23·1	32·0
Water . . .	11·2	10·0	12·1
Oxide of iron .	1·8	1·8	1·4
Lime . . .	...	...	0·4
Magnesia . .	0·8	0·9	
Potash } Soda } . .	1·9		
	99·9	99·9	99·6

The silicate of alumina also constitutes the chief portion of several other very important mineral substances, among which may be mentioned *slate*, *fuller's earth*, and *pumice-stone*. *Marl* is clay containing a considerable quantity of carbonate of lime. *Loam* is also an impure variety of clay. The different varieties of *ochre*, as well as *umber* and *sienna*, are simply clays coloured by the oxides of iron and manganese.

ALUM, which is the chief compound of aluminum employed in the arts, is always obtained either from clay or slate, but there are several processes by which it may be manufactured.

The simplest process is that in which pipe-clay, or some other clay containing very little iron, is calcined, ground to powder, and heated on the hearth of a reverberatory furnace with half its weight of sulphuric acid, until it becomes a stiff paste, which is then exposed to air for several weeks. During this time the alumina of the clay enters into combination with the sulphuric acid to form sulphate of alumina, which may be obtained by washing the mass with water, when the sulphate of alumina dissolves, and the undissolved silicic acid (still retaining a portion of the alumina) is left. When the solution containing the sulphate of alumina is evaporated to a syrupy consistence and allowed to cool, it solidifies into a white crystalline mass, which is used by dyers under the erroneous name *concentrated alum*. The sulphate of alumina can be obtained in crys-

containing $Al_2O_3 . 3SO_3 + 18Aq.$, but there is considerable difficulty btaining these crystals on account of the extreme solubility of the It is on account of this circumstance that the sulphate of alumina sually converted into alum, which admits of very easy crystallisation purification. In order to transform the sulphate of alumina into m, its solution is mixed with sulphate of potash, when, by suitable poration, beautiful octahedral crystals are obtained, having the compo- ion $Al_2O_3 . 3SO_3, KO . SO_3 + 24Aq.$

Alum is more commonly prepared from the mineral termed *alum-shale*, hich contains silicate of alumina, together with a considerable quantity finely-divided iron pyrites and some bituminous matter. This shale coarsely broken up, and built into long pyramidal heaps, together with ternate layers of coal, unless the shale should happen to contain a suffi- nt amount of bitumen. These heaps are set fire to in several places, d are partly smothered with spent ore in order to prevent too great a se of temperature. During this slow roasting of the heap, the iron yrites (FeS_2) loses half its sulphur, which is converted by burning into lphurous acid (SO_2), and this, in contact with the porous shale and the mospheric oxygen, becomes converted into sulphuric acid (p. 200). his latter acid combines with the alumina to produce sulphate of alumina. he roasted heap is then allowed to remain for some months exposed to e air, and moistened from time to time, in order to promote the absorp- n of oxygen by the sulphide of iron (FeS), and its conversion into sul- ate of iron ($FeO . SO_3$). The heap is afterwards lixiviated with water, hich dissolves out the sulphates of alumina and iron, together with some lphate of magnesia, which has also been formed in the process. When is *crude alum liquor* is evaporated to a certain extent, a large quantity sulphate of iron (green vitriol) crystallises out, and the liquid from hich these crystals have separated is then mixed with so much solu- n of chloride of potassium as a preliminary experiment has shown to necessary to yield the largest amount of alum. The chloride of potas- m is obtained as soap-boiler's waste, and as the refuse from saltpetre neries and glass-houses. The sulphate of iron still left in the solu- n is decomposed by the chloride of potassium, yielding chloride of n and sulphate of potash, which combines with the sulphate of alumina form alum. If there be much sulphate of magnesia in the liquor, it is bsequently obtained in crystals and sent into the market.

Where sulphate of ammonia can be obtained at a cheap rate (as in the ghbourhood of the gas-works), it is very commonly substituted for the loride of potassium, when *ammonia-alum* is obtained instead of *potash- m*. The former is similar in all respects to the latter salt, except that ontains the hypothetical metal ammonium (NH_4) in place of potassium, d its formula is, therefore, $Al_2O_3 . 3SO_3, NH_4O . SO_3 + 24$ Aq.

For all the uses of alum, in dyeing and calico-printing, in paper-making d in the manufacture of colours, ammonia-alum answers quite as well potash-alum, and hence both these salts are sold under the common ne of alum.

These alums are the representatives of an important class of double phates, composed of a sulphate of one of the alkalies combined with normal sulphate of a sesquioxide. They all contain 24 eqs. of water crystallisation, and their crystalline form is that of the cube or octa- lron.

When a solution of alum is mixed with a little solution of carbonate of

soda, a precipitate of alumina is formed, which redissolves when the solution is stirred. If the addition of carbonate of soda be continued as long as the precipitate redissolves when stirred, the salt $Al_2O_3 . SO_3$ will remain in the solution—

$$Al_2O_3 . 3SO_3, KO . SO_3 + 2(NaO . CO_2) = Al_2O_3 . SO_3 + 2(NaO . SO_3) + KO . SO_3 + 2CO_2 .$$

This solution of *basic alum*, as it is called, is decomposed by boiling, alumina being deposited and ordinary alum remaining in solution—

$$3(Al_2O_3 . SO_3) + KO . SO_3 = 2Al_2O_3 + Al_2O_3 . 3SO_3, KO . SO_3 .$$

When stuffs are immersed in the solution of basic alum they also withdraw a portion of alumina, which becomes fixed in their fibre, and serves as a mordant to attract and fix the colouring matter when the stuff is transferred to a dye-bath.

Alumina.—When ammonia-alum is strongly heated, it loses the whole of its water, ammonia,* and sulphuric acid, leaving merely a white insoluble earthy substance which is alumina itself (Al_2O_3), and differs widely from the metallic oxides which have been hitherto considered, by the feebly basic character which it exhibits. Not only is alumina destitute of alkaline properties, but it is not even capable of entirely neutralising the acids, and hence both sulphate of alumina and alum are exceedingly acid salts.

Pure crystallised alumina is found in nature as the mineral *corundum*, distinguished by its extreme hardness, in which it ranks next to the diamond. An opaque and impure variety of corundum constitutes the very useful substance *emery*. The *ruby* and *sapphire*† consist of nearly pure alumina; *spinelle* is a compound of magnesia with alumina, $MgO . Al_2O_3$; whilst in the *topaz* the alumina is associated with silica and fluoride of aluminum. The mineral *diaspore* is a hydrate of alumina ($Al_2O_3 . 2HO$), so named from its falling to powder when heated (διασπορά, *dispersion*).

The artificially prepared hydrate of alumina is characterised by its gelatinous appearance. If a little alum be dissolved in warm water, and some ammonia added to the solution, the ammonia will combine with the sulphuric acid, whilst the alumina will unite with water to form a semi-transparent gelatinous mass of hydrate of alumina ($Al_2O_3 . 3HO$). When washed and dried, it shrinks very much and forms a mass resembling gum. The hydrate of alumina has a great attraction for most colouring matters, with which it forms insoluble compounds called *lakes*. Thus, if a solution of alum be mixed with infusion of *logwood*, and a little ammonia added, the hydrate of alumina will form, with the colouring matter, a purplish-red *lake*, which may be filtered off, leaving the solution colourless. This property is turned to advantage in calico-printing, where the compounds of alumina are largely used as mordants.

Chloride of aluminum.—If the alumina obtained by calcining ammonia-alum be intimately mixed with charcoal, and strongly heated in an earthen tube or retort through which a stream of well-dried chlorine is passed, the oxygen of the alumina is abstracted by the charcoal, to form carbonic

* The great absorption and disappearance of heat during the evaporation of the water and ammonia from this alum, has led to its employment for filling the space between the double walls of fire-proof safes, which may become red-hot outside, whilst the inside is kept below the scorching-point of paper.

† Small crystals of alumina resembling natural sapphire have been obtained by the action of vapour of fluoride of aluminum upon boracic acid at a high temperature. By adding a little fluoride of chromium, crystals similar to rubies and emeralds have been produced.

e, whilst the chlorine combines with the aluminum yielding chloride luminum (Al_2Cl_3) which passes off in vapour and may be condensed, n appropriate receiver, as a white crystalline solid—

$$Al_2O_3 + C_3 + Cl_3 = Al_2Cl_3 + 3CO .$$

his formation of the chloride of aluminum is possessed of some in-st, as an example of the decomposition of a compound body by the peration of two elements, neither of which alone would be able to ompose the compound; neither carbon nor chlorine would, alone, de-mpose alumina, however high the temperature, but when the attraction the carbon for the oxygen is added to that of the chlorine for the minum, the decomposition is easily effected.

But this chloride of aluminum also deserves attention as being the rce from which the metal aluminum may be prepared in large quan-es.

198. *Aluminum.*—In order to obtain this interesting metal, it is only essary to pass the chloride of aluminum in the state of vapour over heated ium, which removes the chlorine in the form of chloride of sodium, ing the aluminum as a white malleable metal about as hard as zinc, fusing at a somewhat lower temperature than silver. For the extrac- of aluminum upon the large scale, the alumina is not prepared from n, but from the mineral known as *Bauxite*, which contains about 67 per t. of alumina, together with peroxide of iron and silica. This mineral eated with soda-ash (*see* p. 265), when carbonic acid escapes, and the a and alumina combine with soda to form silicate of soda, and a ble compound of alumina with soda, which is generally called *alumi-e of soda*, and has the composition $3NaO . Al_2O_3$. On treating the s with water, an insoluble silicate of alumina and soda is left, whilst aluminate of soda is dissolved, and is obtained as an infusible mass en the solution is evaporated. This aluminate of soda is largely used calico-printers as a mordant. To obtain alumina from it, the solution neutralised with hydrochloric acid, which converts the sodium into oride, and precipitates the alumina as hydrate of alumina ($Al_2O_3 . 3HO$). the next step towards the preparation of aluminum, the hydrate of mina is mixed with charcoal and common salt, made up into balls, ed, and strongly heated in earthen cylinders through which dry lorine is passed. The carbon abstracts the oxygen from the alumina, ming carbonic oxide, whilst the aluminum combines with the chlorine, d the chloride of aluminum so formed combines with the chloride of dium, and distils over as the *double chloride of aluminum and sodium* ($Al_2Cl_3 . NaCl$). This salt is then mixed with a proper proportion of etallic sodium, and heated in a reverberatory furnace, when the sodium mbines with the chlorine of the chloride of aluminum, leaving the latter tal to separate in a fused state beneath the melted chloride of sodium, hich protects it from oxidation. The aluminum may be rolled into eets or drawn into wire.

Aluminum is much more sonorous than most other metals. A bar of suspended from a string, and struck with a hammer, emits a clear usical sound. It is remarkable as being the lightest metal capable of sisting the action of air even in the presence of moisture. Its specific avity is 2·5. *This lightness renders it valuable for the manufacture of all weights, such as the grain and its fractions, since these, when made*

of aluminum, are more than three times as large as when made of br and nearly nine times as large as platinum weights of the same denom tion. It is also employed for ornamental purposes, for though not brilliant as silver, it is not blackened by sulphuretted hydrogen, which easily affects that metal (p. 192).

Another characteristic feature of aluminum is its comparative resist to the action of nitric acid even at a boiling heat. No other metal c monly met with, except platinum and gold, is capable of resisting action of nitric acid to the same extent. Hydrochloric acid, how which will not attack gold and platinum, dissolves aluminum with lity, converting it into chloride of aluminum, with disengagement hydrogen; $Al_2 + 3HCl = Al_2Cl_3 + H_3$. Solutions of potash and s also easily dissolve it, forming the so-called aluminates of those alkal thus $3(NaO.HO) + Al_2 = 3NaO.Al_2O_3 + H_3$. Even when strongly heated in air, aluminum is oxidised to a very slight extent, probably because the coating of alumina which is formed remains infus and protects the metal beneath it. For a similar reason, appare aluminum decomposes steam slowly, even at a high temperature.

When aluminum is fused with nine times its weight of copper, it for an alloy very similar to gold in appearance, but almost as strong as ir This alloy was strongly recommended to replace gold for ornamental p poses, but it does not retain its brilliancy so completely as that m Aluminum does not unite with mercury or with melted lead, both which are capable of dissolving nearly all other metals.

199. *Mineral silicates of alumina.*—Many of the chemical formulæ minerals which contain silicates of alumina associated with the silic of other metallic oxides are complicated, from the circumstance that a p of the aluminum is often replaced by iron, which, in the form of sesq oxide (Fe_2O_3), is isomorphous with it, and therefore capable of replac it without altering the crystalline form and general character of th mineral. In a similar manner, the other metals present in the mineral may be exchanged for isomorphous representatives; thus there are two well-known feldspars, potash-feldspar (*orthoclase*) and soda-feldspar (*albite*), having the formulæ $KO.Al_2O_3.6SiO_2$, and $NaO.Al_2O_3.6SiO_2$. These minerals are sometimes mingled in one and the same crystal (*potash-albite* or *pericline*) without bearing any definite equivalent proportion to each other; the formula of such a mineral would be written $(KNa)O.Al_2O_3.6SiO_2$.

Porphyry has the same chemical composition as feldspar.

Mica, again, is composed essentially of magnesia, alumina, and silica ($4MgO.Al_2O_3.4SiO_2$), but part of the magnesium is so constantly replaced by potassium and iron (as protoxide), and part of the aluminum by iron (as sesquioxide), that the general formula for mica must be written $4(KMgFe).(AlFe)_2O_3.4SiO_2$.

Garnet is essentially a double silicate of alumina and lime, but often contains magnesium, iron, or manganese, replacing part of the calcium, and iron replacing part of the aluminum, being written—

$$3(CaMgFeMn)O.(AlFe)_2O_3.3SiO_2.$$

This mineral is sometimes formed artificially in the slag of the iron blast-furnaces.

Chlorite, a very important variety of rock, is a double silicate of alumina and magnesia, with variations as expressed by the formula—

$$4(MgFe)O.(AlFe)_2O_3.2SiO_2.3HO.$$

asalt is a feldspathic rock containing crystals of *augite*—

$$4(CaMgFe)\,O.5SiO_2\,.$$

Gneiss is chemically composed like granite, but the mica is arranged in lar layers. *Trap* rock contains feldspar, together with *hornblende*, ch consists of silicates of alumina, lime, magnesia, and oxide of iron. rnblende is sometimes found replacing the mica in granite, forming the k called *syenite*.

Lapis lazuli, the valuable mineral which furnishes the natural ultra- ine used in painting, consists chiefly of silica and alumina, which con- ute respectively 45 and 32 per cent. of it, but there are also present r cent. of soda, 6 per cent. of sulphuric acid, about 1 per cent. of sul- r, and a somewhat smaller quantity of iron, together with a variable ortion of lime. The cause of its blue colour is not understood, since ner of its predominant constituents is concerned in the production of a colour in other cases. In consequence of the rarity of the mineral, natural ultramarine bears a very high price, but the *artificial ultramarine* anufactured in very large quantities at a low cost, and forms a very imitation. One of the processes for preparing it consists in heating right redness in a covered crucible, for three or four hours, an inti- mixture of 100 parts of pure white clay (kaolin), 100 of dried car- te of soda, 60 of sulphur, and 12 of charcoal. This would be expected ield a mixture of silicate of soda, aluminate of soda, and sulphide of m, the two first being white, and the latter yellow or brown, but the is found to have a *green* colour (*green ultramarine*). It is finely dered, washed with water, dried, mixed with a fifth of its weight of hur, and gently roasted in a thin layer till the sulphur has burnt off, operation being repeated, with fresh additions of sulphur, until the ue has a fine blue colour. In the opinion of some chemists, the pre e of a small proportion of iron is essential to the blue colour, while rs believe the colour to be due to sulphide of sodium or hyposul- e of soda, or both. Ultramarine is a very permanent colour under nary conditions of exposure to air and light, but acids bleach it at , with separation of gelatinous silica and evolution of sulphuretted rogen. Blue writing-paper is often coloured with ultramarine, so that olour is discharged by acids falling upon it in the laboratory. Chlo- also bleaches ultramarine. Starch is often coloured blue with this tance.

Phosphates of alumina are found naturally in several forms. *Turquoise* hydrated phosphate of alumina ($Al_2O_3 . PO_5$), owing its colour to the ence of oxide of copper. *Wavellite* has the composition $3Al_2O_3 . 2PO_5$. e of the earlier analysts detected the phosphoric acid in this mineral, account of the difficulty in separating it from the alumina, so that in comparatively modern chemical works it is described as a hydrate lumina.

00. *Equivalent and atomic weights of aluminum.*—The chloride of minum has been found by analysis to contain 35·5 parts by weight q.) of chlorine, combined with 9·16 parts of aluminum, and if the ride of aluminum be represented as a protochloride (AlCl), the equi- nt of this metal would be 9·16. But when the chloride of aluminum ecomposed by an alkali, it furnishes alumina and a chloride of the li-metal. *If the formula of chloride* of aluminum were really Al ction of potash, for example, upon it must be represented by

equation AlCl + KO = KCl + AlO; so that AlO would represent the formula of alumina. The very strong chemical resemblance of alumina and its salts to *sesquioxide* of iron (Fe_2O_3) and its salts, as well as the isomorphism of these oxides observed in the alums and in many minerals (p. 290), compels the belief that alumina is also a sesquioxide, and that its formula is Al_2O_3. Its formation from the chloride of aluminum by the action of potash must then be represented by—

$$Al_2Cl_3 + 3KO = 3KCl + Al_2O_3$$

so that the chloride of aluminum is a sesquichloride (Al_2Cl_3).

Again, referring to the results of experiment, 3 eqs. (35·5 × 3) of chlorine were found to be combined with 27·48 parts of aluminum, and if this represents 2 eqs., the equivalent of aluminum will be 13·74, though this does not represent correctly the weight of aluminum which displaces 1 part by weight of hydrogen from its compounds (*see* p. 23).

The volume occupied by a definite weight of vapour of aluminum being unknown, the atomic weight of this metal must be deduced from other considerations. The specific gravity (or weight of one volume) of vapour of chloride of aluminum is 9·34. It has been seen that this weight of chloride of aluminum contains 1·92 of aluminum. Hence,

Weight of 1 vol. of chloride of aluminum,		9·34
„	aluminum contained in it,	1·92
„	chlorine „	7·42

Now, 1 vol. of chlorine weighs 2·47, so that 7·42 represents 3 vols. of chlorine; and if it be assumed that 1·92 represents the weight of 1 vol. of aluminum, there are contained, in 1 vol. of chloride of aluminum vapour, 1 vol. or 1 atom of aluminum, and 3 vols. or 3 atoms of chlorine. But it will be remembered that the molecule of a compound body is generally taken to represent 2 vols. (H = 1 vol.), and therefore 1 molecule or 2 vols. of chloride of aluminum vapour would contain 2 vols. or 2 atoms of aluminum, and 6 vols. or 6 atoms of chlorine. These 6 atoms of chlorine represent (35·5 × 6) 213 parts by weight, and are combined, in the chloride, as shown by analysis, with 55·1 parts by weight of aluminum; so that the 2 atoms of aluminum in the chloride represent 55·1 parts by weight, or each atom of aluminum (Al) weighs 27·5, or twice as much as the equivalent accepted above, and the *molecular formula* of the chloride of aluminum must be written Al_2Cl_6. The atomic heat of aluminum supports the assumption of the number 27·5 for its atomic weight. Since, in the chloride of aluminum, the 2 atoms of metal stand to the 6 atoms of chlorine in the place of 6 atoms of hydrogen, 1 atom of aluminum would represent 3 atoms of hydrogen, and the metal would be tri-atomic or ter-equivalent. The atomic formula of alumina would be Al_2O_3 (O = 16).

GLUCINUM.

201. This comparatively rare metal (which derives its name from the sweet taste of its salts, γλυκύς, *sweet*) is found associated with silica and alumina in the *emerald*, which is a double silicate of alumina and glucina, $Al_2O_3 . 3SiO_2$, $3(GlO . SiO_2)$, and owes its colour to the presence of a minute quantity of oxide of chromium. The more common mineral *beryl* has a similar composition, but is of a paler green colour, apparently caused by protoxide of iron. Chrysoberyl consists of glucina and

, also coloured by iron. The earlier analysts of these minerals mistook the for alumina, which it resembles in forming a gelatinous precipitate on addmonia to its solutions, but it is a stronger base than alumina, and is thereable of displacing ammonia from its salts, and of being dissolved by them. ate of ammonia is employed to separate the glucina from alumina, since it dis- the glucina in the cold, forming a double carbonate of glucina and ammonia, which the carbonate of glucina is precipitated on boiling. Glucina (GlO) is mediate in properties between alumina and magnesia, resembling the latter in ndency to absorb carbonic acid from the air, and to form soluble double salts the salts of ammonia, and so much resembling alumina in the gelatinous form s hydrate, its solubility in alkalies, and the sweet astringent taste of its salts, it was formerly regarded as a sesquioxide like alumina.
he metal itself is very similar to aluminum.

02. THORINUM is present in a rare Norwegian mineral, *thorite*, where it is assoed with silica, lime, magnesia, and other metallic oxides. The metal itself is ilar to aluminum, but its oxide *thorina* appears to be a protoxide (ThO), and ers from alumina and glucina in being *insoluble in the alkalies* (potash, for exple), though it dissolves in carbonate of potash. Moreover, the *sulphate of thorina*, paringly soluble in hot water, so that it is precipitated on boiling its solution.

203. YTTRIUM, ERBIUM, and TERBIUM, are very rare metals found in *gadolinite*, a neral silicate occurring at Ytterby in Sweden, and containing beside these, gluum, cerium, and iron. Their oxides, *yttria* (YO), *erbia*, and *terbia*, resemble orina in being insoluble in the alkalies, but soluble in their carbonates; yttria is hite, but erbia has a yellow colour. The salts of yttria and erbia are colourless, at those of terbia are pinkish.

204. CERIUM is also found in gadolinite, but more abundantly in *cerite*, which is ssentially a silicate of cerium. This metal has been employed medicinally, in the rm of oxalate of cerium ($CeO . C_2O_3 . 3HO$). It forms two basic oxides, CeO, which white, and forms colourless salts, and Ce_2O_3, which is yellow, and gives yellow r red salts. In this respect, cerium more nearly resembles iron than aluminum. hese oxides of cerium are insoluble in the alkalies; the protoxide is easily precitated from its salts by oxalic acid in the form of the oxalate mentioned above. esquioxide of cerium does not appear to form a corresponding chloride, but ields protochloride of cerium and free chlorine when heated with hydrochloric cid.

LANTHANIUM (from λανθάνω, *to escape notice*) is also found in cerite, but it differs rom cerium in forming only one oxide (LaO), which is white in the hydrated, but uff in the anhydrous state. When a mixture of nitrates of cerium and lanthanium s calcined, sesquioxide of cerium and oxide of lanthanium are left, and may be eparated by treatment with nitric acid, diluted with 100 parts of water, which dissolves only the latter.

DIDYMIUM (δίδυμος, *twin*) is very similar to lanthanium, which is associated with it n cerite. It also forms but one oxide (DiO), which is violet when hydrated, and rown when anhydrous. It is insoluble in potash. The salts of didymium are either pink or violet.

205. ZIRCONIUM exists in the rare minerals *zircon* and *hyacinth*, in which its oxide *zirconia* (ZrO_2) is combined with silicic acid. Zirconia is somewhat similar to alumina, but is insoluble in potash, and dissolves in carbonate of potash. Its sulphate, moreover, is decomposed by boiling with sulphate of potash, which removes part of the sulphuric acid, forming bisulphate of potash, and precipitates basic sulphate of zirconia. Metallic zirconium somewhat resembles amorphous silicon, but it decomposes water slowly at the boiling point, and has not been fused.

ZINC.

206. Zinc occupies a high position among useful metals, being peculi… fitted, on account of its lightness, for the construction of gutters, wa… pipes, and roofs of buildings, and possessing for these purposes a g… advantage over lead, since the specific gravity of the latter metal is ab… 11·5, whilst that of zinc is only 6·9. For such applications as these, wh… great strength is not required, zinc is preferable to iron, on account of i… superior malleability; for although a bar of zinc breaks under the ha… mer at the ordinary temperature, it becomes so malleable at 250° F. as t… admit of being rolled into thin sheets. This malleability of zinc wh… heated was discovered only in the commencement of this century, un… which time the only use of the metal was in the manufacture of bra… When zinc is heated to 400° F., it again becomes brittle. The ea… fusibility of zinc also gives it a great advantage over iron, as rendering it… easy to be cast into any desired form; indeed, zinc is surpassed in… fusibility (among the metals in ordinary use) only by tin and lead, its… melting point being below a red heat, and usually estimated at 770° F. Zinc is also less liable than iron to corrosion under the influence of moist… air, for although a bright surface of zinc soon tarnishes when exposed to… the air, it merely becomes covered with a thin film of oxide of zinc (pass… ing gradually into basic carbonate, by absorption of carbonic acid from the… air) which protects the metal from further action.

The great strength of iron has been ingeniously combined with the… durability of zinc, in the so-called *galvanised iron*, which is made by coat… ing clean iron with melted zinc, thus affording a protection much needed… in and around large towns, where the sulphurous and sulphuric acids… arising from the combustion of coal, and the acid emanations from various… factories, greatly accelerate the corrosion of unprotected iron. The iron… plates to be coated are first thoroughly cleansed by a process which will be… more particularly noticed in the manufacture of tin-plate, and are then… dipped into a vessel of melted zinc, the surface of which is coated with… sal-ammoniac (hydrochlorate of ammonia) in order to dissolve the oxide of… zinc which forms upon the surface of the melted metal, and might adhere… to the iron plate so as to prevent its becoming uniformly coated with the… zinc ($ZnO + NH_3.HCl = ZnCl + NH_3 + HO$). A more firmly ad… herent coating of zinc is obtained by first depositing a thin film of tin… upon the surface of the iron plate by galvanic action, and hence the name… of *galvanised* iron.

The ores of zinc are found pretty abundantly in England, chiefly in the… Mendip Hills in Somersetshire, at Alston Moor in Cumberland, in Corn… wall and Derbyshire, but the greater part of the zinc used in this country… is imported from Belgium and Germany, being derived from the ores of… Transylvania, Hungary, and Silesia.

Metallic zinc is never met with in nature. Its chief ores are *calamine* or carbonate of zinc ($ZnO.CO_2$), *blende* or sulphide of zinc (ZnS), and *red zinc ore*, in which oxide of zinc (ZnO) is associated with the oxides of iron and manganese.

Calamine is so called from its tendency to form masses resembling a… bundle of reeds (*calamus, a reed*). It is found in considerable quantities… Somersetshire, Cumberland, and Derbyshire. The mineral known as… *silicic calamine* is a silicate of zinc ($2ZnO.SiO_2.HO$). Blende derives

name from the German *blenden*, *to dazzle*, in allusion to the brilliancy its crystals, which are generally almost black from the presence of sulide of iron, the true colour of pure sulphide of zinc being white. ende is found in Cornwall, Cumberland, Derbyshire, Wales, and the e of Man, and is generally associated with galena or sulphide of lead, hich is always carefully picked out of the ore before smelting it, since it ould become converted into oxide of lead, which corrodes the earthen ucibles employed in the process.

In England, the extraction of zinc from its ores is carried on chiefly at ristol, Birmingham, and Sheffield. Before extracting the metal from ese ores, they are subjected to a preliminary treatment which brings em both to the condition of oxide of zinc. For this purpose the calamine is simply calcined in a reverberatory furnace, in order to expel the rbonic acid; but the blende is *roasted* for ten or twelve hours with conant stirring, so as to expose fresh surfaces to the air, when the sulphur sses off in the form of sulphurous acid, and its place is taken by the xygen, the ZnS becoming ZnO. The extraction of the metal from this xide of zinc depends upon the circumstance that zinc is capable of being istilled at a bright red heat, its boiling point being 1904° F.

The facility with which this metal passes off in the form of vapour is en when it is melted in a ladle over a brisk fire, for at a bright red at abundance of vapour rises from it, which, taking fire in the air, burns ith a brilliant greenish white light, throwing off into the air numerous hite flakes of light oxide of zinc (the philosopher's wool, or *nil album* the old chemists).

The distillation of zinc may be effected on the small scale in a black-lead crucible , fig. 224) about 5 inches high and 3 in diameter. A hole is drilled through the ttom with a round file, and into this is fitted a piece wrought-iron gas-pipe (B) about 9 inches long and 1 ch wide, so as to reach nearly to the top of the inside the crucible. Any crevices between the pipe and the des of the hole are carefully stopped up with fire-clay istened with solution of borax. A few ounces of zinc e introduced into the crucible, the cover of which is en carefully cemented on with fire-clay (a little borax eing added to bind it together at a high temperature), nd the hole in the cover is stopped up with fire-clay. he crucible having been kept for several hours in a arm place, so that the clay may dry, it is placed in a ylindrical furnace with a hole at the bottom, through hich the iron pipe may pass, and a lateral opening to which is inserted an iron tube (C) connected with forge bellows. Some lighted charcoal is thrown into he furnace, and when this has been blown into a blaze, he furnace is filled up with coke broken into small eces. The fire is then blown till the zinc distils freely to a vessel of water placed for its reception. Four nces of zinc may be easily distilled in half-an-hour.

Fig. 224.—Distillation of zinc.

English method of extracting zinc.—The oxide of zinc, obtained as above m calamine or blende, is mixed with about half its weight of coke or anracite coal. This mixture is introduced into large crucibles (fig. 225) with ole in the bottom, through which passes a short wide iron pipe destined the passage of the vapour of zinc. These crucibles are about 4 feet high $2\frac{1}{2}$ feet wide. Some large pieces of coke are first introduced into them prevent the charge from passing into the iron pipes, and when they have *n charged with the above mixture*, their covers are cemented on, and

they are heated in furnaces somewhat resembling those of a glass-h each furnace receiving six crucibles, which generally contain, in al ton of roasted ore. When the mixture in the crucibles is heated t ness, it begins to evolve carbonic oxide, produced by the combinat the carbon with the oxygen from the oxide of zinc. This gas burns a blue flame at the mouth of the iron pipe; but at a bright red he metallic zinc which has been thus liberated is converted into vapou the greenish-white flame of burning zinc is perceived at the o When this is the case, about 8 f iron pipe are joined on to the piece, in order to condense the v of zinc, which falls into a vessel for its reception. The distillation pies about sixty hours, and the a yield is about 35 parts of zinc fro of ore, a considerable quantity o being left behind in the form of s of zinc (electric calamine), which reduced by distillation with carbo

Fig. 225.—English zinc furnace.

The zinc thus obtained, howe mixed with a considerable quan oxide of zinc, and with other matters carried over from the cru It is, therefore, again melted in iron pan, and allowed to rest, in that the dross may rise to the s this is skimmed off, to be worke again in a fresh operation, and the is cast into ingots, which are sent into commerce under the na *spelter*.

Belgian process for the extraction of zinc.—At the Vieille-Mo works, near Liége, calamine is exposed to the rain for several mon order to wash out the clay; it is then calcined t the water and carbonic acid, the oxide of zinc tained being mixed with half its weight of coa and distilled in fire-clay cylinders (C, fig. 226) ing about 40 lbs. each, and set in seven tiers each in the same furnace, the vapour of zinc conveyed by a short conical iron pipe (B) conical iron receiver (D), which is emptied eve hours into a large ladle, from which the zinc is into ingot-moulds. Each distillation occupies twelve hours. The advantage of this particula of arranging the cylinders is, that it economis by allowing the poorer ores, which require les to distil all the zinc from them, to be introduc the upper rows of cylinders farthest from the fi There are two varieties of Belgian ore, one con 33 and the other 46 per cent. of zinc, but a large proportion of thi the form of silicate, which is not extracted by the distillation.

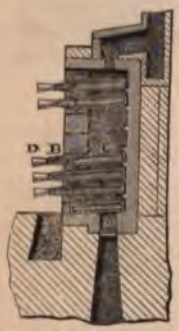


Fig. 226.—Belgian zinc furnace.

Silesian process for extracting zinc.—In Silesia, the oxide of zi ained by the calcination of calamine is mixed with fine cinders, a illed in arched earthen retorts (A, fig. 227), into which the ch

ced through a small door (B), which is then cemented up. These are arranged in a double row in the same furnace (fig. 228), and our of zinc is con- in a bent earthen- pe attached to each and having an (C) near the bend, is kept closed, un- s necessary to clear pipe. In regard onsumption of fuel, this process is far more economical than that l in this country. The Silesian zinc is remelted, before casting gots, in clay in- f iron pots, since zinc always dis- iron, and a very quantity of that s found to injure hen required for into sheets.

Fig. 227.

Fig. 228.—Silesian zinc furnace.

nall quantity of ways distils over r with the zinc, ce this metal also es with the roll- zinc into sheets, n of it is separated from zinc intended for this purpose, by melting lter, in large quantity, upon the hearth of a reverberatory furnace, of which is inclined so as to form a deep cavity at the end nearest mney. The specific gravity of lead being 11·4, whilst that of zinc the former accumulates chiefly at the bottom of the cavity, and ots cast from the upper part of the melted zinc will contain but ad.

ts of zinc, when broken across, exhibit a beautiful crystalline frac- hich, taken in conjunction with the bluish colour of the metal, it to be easily identified.

spelter of commerce is liable to contain lead, iron, tin, antimony, copper, and cadmium.

being easily dissolved by diluted acids, it is necessary to be care- mploying this metal for culinary purposes, since its soluble salts sonous.

ill be remembered that the action of diluted sulphuric acid upon employed for the preparation of hydrogen. Pure zinc, however, hydrogen very slowly, since it becomes covered with a number of en bubbles which protect it from further action; but if a piece of or platinum be made to touch the zinc beneath the acid, these being electronegative towards the zinc, will attract the [illegible] drogen, leaving the zinc free from bubbles and [illegible] to the action of the acid, so that a continuous dis en is maintained. As a curious illustration of this m or silver foil may be [illegible] to sink in dilut- *comes in contact with* [illegible] inc, when the

gen bring it up to the surface. The lead, iron, &c., met with in commercial zinc are electronegative to the zinc, and thus serve to maintain a constant evolution of hydrogen.

A coating of metallic zinc may be deposited upon copper by slow galvanic action, if the copper be immersed in a concentrated solution of potash, at the boiling point of water, in contact with metallic zinc, when a portion of the latter is dissolved in the form of oxide, with evolution of hydrogen, and is afterwards precipitated on the surface of the electronegative copper.

Oxide of zinc.—Zinc forms but one oxide, which is known in commerce as *zinc-white*, and is prepared by allowing the vapour of the metal to burn in earthen chambers through which a current of air is maintained. This zinc-white is sometimes used for painting in place of white lead (carbonate of lead), over which it has the advantages of not injuring the health of the persons using it, and of being unaffected by sulphuretted hydrogen, an important consideration in manufacturing towns where that substance is so abundantly supplied to the atmosphere. Unfortunately, however, the oxide of zinc does not combine with the oil of the paint, as oxide of lead does, and the paint is consequently more liable to peel off. The oxide of zinc has the characteristic property of becoming yellow when heated, and white again as it cools. It is sometimes used in the manufacture of glass for optical purposes.

Oxide of zinc forms a soluble compound with potash, in this respect resembling alumina, and therefore metallic zinc, like aluminum, is dissolved by boiling with solution of potash, hydrogen being disengaged from the water, the oxygen of which combines with the zinc.

The *sulphate of zinc* or *white vitriol*, which is employed in medicine and more extensively in calico-printing, is prepared by roasting blende (sulphide of zinc, ZnS) at a low temperature, when both its elements combine with oxygen, the oxide of zinc and sulphuric acid thus produced remaining in combination as sulphate of oxide of zinc ($ZnO . SO_3$). After roasting, the mass is treated with water, which dissolves the sulphate, and yields it again, on evaporation, in prismatic crystals having the formula $ZnO . SO_3 . HO + 6Aq$.

Chloride of zinc (ZnCl), prepared by dissolving zinc in hydrochloric acid, is known in commerce as *Burnett's disinfecting fluid*, since it is capable of absorbing hydrosulphuric acid, ammonia, and other offensive products of putrefaction, and arrests the decomposition of wood and animal substances. By evaporating its solution, the chloride of zinc is obtained in a fused state, and solidifies on cooling into white deliquescent masses. It has a very powerful attraction for water.

207. *Equivalent and atomic weights of zinc.*—When zinc is dissolved in hydrochloric acid, 32·5 parts by weight of zinc displace 1 part of hydrogen; hence 32·5 represents the equivalent of zinc. Considerations similar to those referred to in the case of magnesium (p. 284) have induced most chemists to regard the atomic weight of zinc as 65, or double its equivalent, so that zinc is a bi-equivalent or di-atomic metal, and the *atomic formula* of its oxide is $\dot{Z}n\dot{O}$, ($\dot{Z}n = 65$, $\dot{O} = 16$), and that of its chloride $\dot{Z}nCl_2$.

CADMIUM.

metal is found in small quantities in the ores of zinc, its
g indicated during the extraction of that metal (p. 296) by
e of a brown flame (*brown blaze*) at the commencement of
n, before the characteristic zinc-flame (*blue blaze*) is seen at
the iron tube. Cadmium is more easily vaporised than zinc
80° F.), so that the bulk of it is found in the first portions
d metal. If the mixture of cadmium and zinc be dissolved
lphuric acid, and the solution treated with hydrosulphuric
ight yellow precipitate of *sulphide of cadmium* (CdS) is ob-
is employed in painting under the name of *cadmia*. By
is in strong hydrochloric acid and adding carbonate of am-
rbonate of cadmium ($CdO . CO_2$) is precipitated, from which
ium may be extracted by distillation with charcoal.
esembling zinc in its volatility and its chemical relations, in
is much more similar to tin, and emits a crackling sound
l when bent. Like tin, also, it is malleable and ductile at
temperature, and becomes brittle at about 180° F. It is
ible than tin, becoming liquid at 242° F., so that it is useful
sible alloys. An alloy of 3 parts of cadmium with 15 of
lead, and 4 of tin, fuses at 140° F. In its behaviour with
alies cadmium is similar to zinc, but the metal is easily dis-
m all others by its yielding a characteristic chestnut-brown
eated in air. This oxide (CdO) is the only oxide of cadmium.
of cadmium (CdI), obtained by the action of iodine upon
the presence of water, is employed in photography.
lent weight of cadmium, deduced from the analysis of its
6. The specific gravity (or weight of one volume) of vapour
s 3·94, or 57 times that of hydrogen. If one vol. of hydro-
ented as 1 atom, weighing 1, then 1 vol. of cadmium vapour
would weigh 57; or allowing for error in the troublesome
f determining the specific gravity of its vapour, the atom of
ld be represented by a number identical with its equivalent
specific heat of cadmium, however, as well as its general
tions, favour the view that it is a di-atomic metal like zinc,
ight being 112.

e name of a metal which has recently been discovered, with the help
ope, in a specimen of blende from Freiberg. Its name refers to an
e in the spectrum. The examination of the metal is as yet imper-
white, malleable, and dissolves, like zinc and cadmium, in hydro-
Its specific gravity is 7·36. To extract indium from the Freiberg
is boiled with dilute sulphuric acid, employed in such quantity as to
e zinc undissolved, together with indium and lead. The residue is
ric acid, the lead and cadmium precipitated by hydrosulphuric acid,
elled by boiling, and the oxide of indium precipitated from the
bonate of baryta. When this precipitate is dissolved in hydrochloric
s of ammonia added, the white hydrated oxide of indium is precipi-
be reduced by heating in hydrogen.
ed heat it burns with a violet blue flame, yielding a yellow oxide of

nt of indium appears to be about 36.

M.—This is a rare metal, never employed in the metallic state. I
sesquioxide (U_2O_3) and black oxide ($2UO . U_2O_3$), for impu

yellow and black colours respectively to glass and porcelain. The chief sour these compounds is the mineral *pitch-blende*, which contains a large proporti black oxide of uranium, together with silica, iron, copper, lead, and arsenic. I chemical relations uranium presents some similarity to iron and manganese, forms two distinct oxides, UO and U_2O_3, of which the former is decidedly b whilst the latter is capable of acting both as an acid and a base. The b greenish-yellow colour of the salts of the sesquioxide of uranium is characteris the metal, and glass coloured with this oxide exhibits the remarkable optical of fluorescence in a very high degree.

IRON.

210. This most useful of all metals is one of those most widely abundantly diffused in nature. It is to be found in nearly all form rock, clay, sand, and earth, its presence in these being commonly i cated by their colours, for iron is the commonest of natural min colouring ingredients. It is also found, though in small proportion plants, and in larger quantity in the bodies of animals, especially in blood, which contains about 0·5 per cent. of iron in very intimate as ation with its colouring matter.

But iron is very rarely found in the metallic state in nature, b almost invariably combined either with oxygen or sulphur.

Metallic iron is met with, however, in the *meteorites* or metallic mas sometimes of enormous size, and of unknown origin, which occasion fall upon the earth. Of these iron is the chief component, but these also generally present, cobalt, nickel, chromium, manganese, copper, magnesium, carbon, phosphorus, and sulphur.

The chief forms of combination in which iron is found in sufficie abundance to render them available as sources of the metal, are shown the following table :—

Ores of Iron.

Common Name.	Chemical Name.	Composition.
Magnetic iron ore	Protosesquioxide of iron	Fe_3O_4
Red hæmatite	Sesquioxide of iron	Fe_2O_3
Specular iron	" "	"
Brown hæmatite	Hydrated sesquioxide	$2Fe_2O_3.3HO$
Spathic iron ore	Carbonate of iron	$FeO.CO_2$
Clay iron-stone	Carbonate of iron with clay	
Blackband	Carbonate of iron with clay and bituminous matter	
Iron pyrites	Bisulphide of iron.	FeS_2

These ores are frequently associated with extraneous minerals, som the constituents of which are productive of injury to the quality of iron. It is worthy of notice that scarcely one of the ores of iro entirely free from sulphur and phosphorus, substances which will be f to have a very serious influence on the quality of the iron extracted f them, and the presence of which increases the difficulty of obtaining metal in a marketable condition.

The following table illustrates the general composition of the most portant English ores of iron, with reference to the proportions of iron, of those substances which materially influence the character of the

cted from the ore, viz., manganese (present as oxide or carbonate), phorus (present as phosphoric acid), and sulphur (present as bisul- e of iron). The maximum and minimum quantities found in each re specified.

*British Iron Ores.**

In 100 parts.	Iron.		Oxide of Manganese.		Phosphoric Acid.		Bisulphide of Iron. (Pyrites.)		No. of Samples Analysed.
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	
ron-stone from coal-measures,	43·30	20·95	3·30	0·46	1·42	0·07	1·21	0	77
iron-stone from the lias,	49·17	17·34	1·30	0	5·05	0	1·60	0	12
n hæmatite,	63·04	11·98	1·60	trace	3·17	0	0·30	0	23
hæmatite,	69·10	47·47	1·13	trace	trace	trace	0·06	0	5
hic ore,	49·78	13·98	12·64	1·93	0·22	0	0·11	0	6
etic ore,	57·01		0·14		0·10		0·07		1

rom this table it will be gathered that, among the most abundant of iron ores of this country, red hæmatite is the richest and purest, lst the brown hæmatite often contains considerable proportions of hur and phosphorus, and the spathic ore, though containing little hur and phosphorus, often contains much manganese.

he argillaceous ores, or clay iron-stones, found in the lias contain more sphoric acid than those from the coal-measures; and these latter, as a eral rule, contain more sulphur (pyrites) than the former, although the ximum in the table does not show this.

Clay iron-stone is the ore from which the largest quantity of iron is racted in England, since it is found abundantly in the coal-measures Staffordshire, Shropshire, and South Wales, and it is a circumstance great importance in the economy of English iron-smelting, that the l and limestone required in the smelting process, and even the fire-clay ployed in the construction of the furnace, are found in the immediate inity of the ore.

Blackband is the clay iron-stone found in the coal-fields of Scotland, l often contains between 20 and 30 per cent. of bituminous matter, ich contributes to the economy of fuel in smelting it.

Red hæmatite (Fe_2O_3) is the most characteristic of the ores of iron, urring in hard shining rounded masses, with a peculiar fibrous structure a dark red-brown colour, whence the ore derives its name (*αἷμα, blood*). s found in considerable quantities in Lancashire and Cornwall, but un- unately its very compact structure is an obstacle to its being smelted ıe, so that it is generally mixed with some clay iron-stone, and hence iron obtained is not so free from sulphur and phosphorus as if it were racted from hæmatite alone.

ed ochre is a soft variety of this ore, containing a little clay.

Brown hæmatite ($2Fe_2O_3 . 3HO$) is found at Alston Moor (Cumber- l) and in Durham, but it is more abundant on the Continent, and is source of most of the Belgian and French irons. *Pea iron ore* and *w ochre* are varieties of brown hæmatite. The Scotch ore which is ed *kidney-form clay iron-stone* is really a hydrated sesquioxide of iron

* *This table has been compiled from the analyses given in "Percy on Iron and Steel.*

Specular iron ore (Fe_2O_3) (*oligist ore* or *iron-glance*), although of the same composition as red hæmatite, is very different from it in appearance, having a steel-grey colour and a brilliant metallic lustre. The island of Elba is the chief locality where this ore is found, but it also occurs in Germany, France, and Russia. The excellent quality of the iron smelted from this ore is due partly to the purity of the ore, and partly to the circumstance that charcoal, and not coal, is employed in smelting it.

Magnetic iron ore (Fe_3O_4), of which the *loadstone* is a variety, has a more granular structure, and a dark iron-grey colour. It forms mountainous masses in Sweden, and is also found in Russia and North America. It is generally smelted with charcoal, and yields an excellent iron. *Iron sand*, a peculiar heavy black sand, of metallic lustre, consists in great measure of the magnetic ore, but contains a very large proportion of titanic acid. It is found abundantly in India, Nova Scotia, and New Zealand; but its fine state of division prevents it from being largely available as a source of iron.

Spathic iron ore ($FeO.CO_2$) is found in abundance in Saxony, and often contains a considerable quantity of carbonate of manganese, which influences the character of the metal extracted from it.

The *oolitic iron ore*, occurring in the Northampton oolite, contains both hydrated sesquioxide and carbonate of iron, together with clay.

Iron pyrites (FeS_2) is remarkable for its yellow colour, its brilliant metallic lustre, and crystalline structure, being generally found either in distinct cubical or dodecahedral crystals, or in rounded nodules of radiated structure. It was formerly disregarded as a source of iron, on account of the difficulty of separating the sulphur; but since the demand for iron has so largely increased, an inferior quality of the metal has been extracted from the residue left after burning the pyrites in the manufacture of oil of vitriol (p. 203), the residue being first well roasted in a lime-kiln to remove as much as possible of the sulphur.

211. *Metallurgy of iron.*—Iron owes the high position which it occupies among useful metals to a combination of valuable qualities not met with in any other. Although possessing nearly twice as great *tenacity* or *strength* as the strongest of the other metals commonly used in the metallic state, it is yet one of the lightest, its specific gravity being only 7.7, and is therefore particularly well adapted for the construction of bridges and large edifices, as well as for ships and carriages. It is the least yielding or malleable of the metals in common use, and can therefore be relied upon for affording a rigid support; and yet its ductility, when heated, is such that it admits of being rolled into the thinnest sheets and drawn into the finest wire, the strength of which is so great that a wire of $\frac{1}{16}$th inch in diameter is able to sustain 705 pounds, while a similar wire of copper, which stands next in order of tenacity, will not support more than 385 pounds.

Being, with the exception of platinum, the least fusible of useful metals, iron is applicable to the construction of fire-grates and furnaces. Nor are its qualifications all dependent upon its physical properties, for it not only enters into a great number of compounds which are of the utmost use in the arts, but its chemical relations to one of the non-metallic elements, carbon, are such, that the addition of a small quantity of this element converts it into *steel*, far surpassing iron in the valuable properties of hardness and elasticity; whilst a larger quantity of carbon gives rise to cast

, the greater fusibility of which permits it to be moulded into vessels
l shapes which could not be produced by forging.

212. *English process of smelting clay iron-stone.* — The first step
wards the extraction of the metal consists in calcining (or *roasting*) the
in order to expel the water and carbonic acid which it contains. To
ect this the ore is built up, together with a certain amount of small
al, into long pyramidal heaps, resting upon a foundation of large lumps
coal; blackband often contains so much coal that any further addition
unnecessary. These heaps are kindled in several places, and allowed to
rn slowly until all the fuel is consumed. This calcination has the effect
rendering the ore more porous, and better fitted for the smelting pro-
ss. If the ore contained much sulphur, a part of it would be expelled
the roasting, in the form of sulphurous acid.

Sometimes the calcination is effected in kilns resembling lime-kilns,
d it is often altogether omitted as a separate process, the expulsion of
e water and carbonic acid being then effected in the smelting-furnace
elf as the ore descends.

The calcined ore is smelted in a huge *blast-furnace* (fig. 229) about fifty or
ty feet high, built of massive masonry, and lined internally with fire-brick.

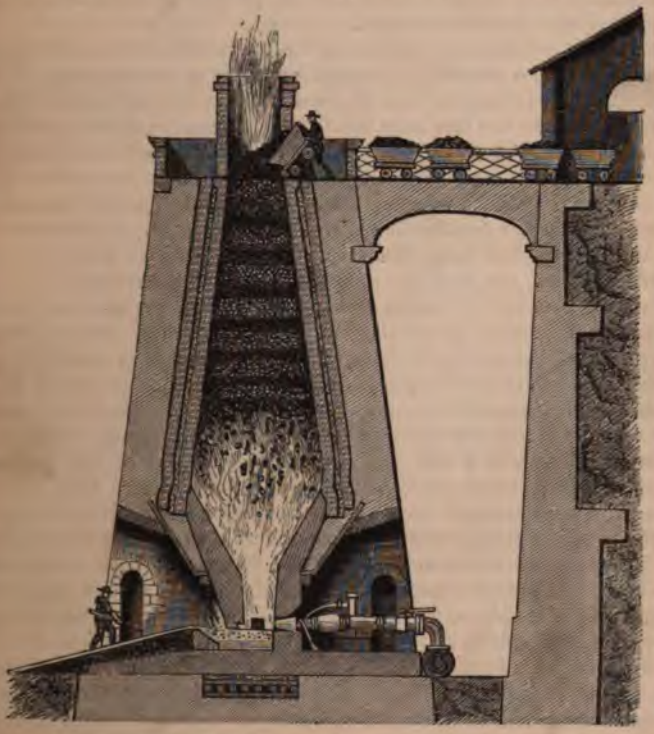


Fig. 229.—Blast-furnace for smelting iron ores.

ce it would be impossible to obtain a sufficiently high temperature with
natural draught of this furnace, air is forced into it at the bottom,
er a pressure of three or four pounds upon the inch, through three

tuyère pipes, the nozzles of which pass through apertures in three of the furnace. It would be very easy to reduce to the metallic state oxide of iron contained in the calcined ore, by simply throwing it into furnace, together with a proper quantity of coal, coke, or charcoal; the metallic iron fuses with so great difficulty, that it is impossible to rate it from the clay unless this latter is brought into a liquid state; even then the fusion of the iron, which is necessary for complete se tion, is only effected after it has formed a more easily fusible compo with a small proportion of carbon derived from the fuel.

Now, clay is even more difficult to fuse than iron, so that it is n sary to add, in the smelting of the ore, some substance capable of for with the clay a combination which is fusible at the temperature of furnace. If clay (silicate of alumina) be mixed with limestone (carbo of lime), and exposed to a high temperature, the carbonic acid is exp from the limestone, and the lime unites with the clay, forming a do silicate of alumina and lime, which becomes perfectly liquid, and w cool, solidifies to a glass or *slag*. The limestone is here said to act *flux*, because it induces the clay to *flow* in the liquid state. In o therefore, that the clay may be readily separated from the metallic i the calcined ore is mixed with a certain proportion of limestone b being introduced into the furnace.

Great care is necessary in first lighting the blast-furnace lest the masonry should be cracked by too sudden a rise of temperature, and w once lighted, the furnace is kept in constant work for years until in wa repair. When the fire has been lighted, the furnace is filled up with and as soon as this has burnt down to some distance below the chimn layer of the mixture of calcined ore with the requisite proportion of stone is thrown upon it; over this there is placed another layer of coke, a second layer of the mixture of ore and flux, and so on, in alternate l until the furnace has been filled up; when the layers sink down, quantities of fuel, ore, and flux are added, so that the furnace is kept stantly full. As the air passes from the tuyère pipes into the bott the furnace, it parts with its oxygen to the carbon of the fuel, wh converts into carbonic acid (CO_2); the latter, passing over the re fuel as it ascends in the furnace, is converted into carbonic oxide (C combining with an additional quantity of carbon. It is this car oxide which reduces the calcined ore to the metallic state, when it in contact with it, at a red heat, in the upper part of the furnac carbonic oxide removes the oxygen, at a high temperature, from the of iron, and becomes carbonic acid, the iron being left in the metallic But the iron so reduced remains disseminated through the mass until it has passed down to a part of the furnace which is more str heated, where the iron enters into combination with a small proport carbon to form cast-iron, which fuses and runs down into the *cruci* cavity for its reception at the bottom of the furnace. At the same the clay contained in the ore is acted upon by the lime of the flux ducing a double silicate of alumina and lime, which also falls in the state into the crucible, where it forms a layer of "slag" above the h metal. This slag, which has five or six times the bulk of the ir allowed to accumulate in the crucible, and to run over its edge dow incline (or *cinder-fall*) upon which the blast-furnace is built; but a sufficient quantity of cast-iron has collected at the bottom of the cru is run out through a hole provided for the purpose, either into o

a bed of sand or into iron moulds, where it is cast into rough
indrical masses called *pigs*, whence cast-iron is also spoken of as
The temperature of the furnace is, of course, highest in the
te neighbourhood of the tuyères; the reduction of the iron to the
state appears to commence at about two-thirds of the way down
ace, the volatile matters of the ore, fuel, and flux being driven off
is point is reached.
idea may be formed of the immense scale upon which the smelt-
ron ores is carried out, when it is stated that each furnace con-
n the course of twenty-four hours, about 50 tons of coal, 30 tons
tons of limestone, and 100 tons of air. The cast-iron is run off
e crucible once or twice in twelve hours, in quantities of five
ns at a time. The average yield of calcined clay iron-stone is 35
of iron.
ases escaping from the chimney of the blast-furnace are highly
ble, for they contain, beside the nitrogen of the air blown into the
a considerable quantity of carbonic oxide and some hydrogen,
with the carbonic acid formed by the action of the carbonic oxide
ore. Since the carbonic oxide and hydrogen confer considerable
power upon these gases, they are employed in some iron-works for
team boilers, or for calcining the ore, or for raising the temperature
last.

mposition of the gas issuing from a hot-blast furnace (fed with uncoked
be judged of from the following table:—

Gas from Blast-Furnace.

Nitrogen, . . .	55·35 vols.
Carbonic oxide, . .	25·97 „
Hydrogen, . . .	6·73 „
Carbonic acid, . .	7·77 „
Marsh-gas, . .	3·75 „
Olefiant-gas, . .	0·43 „
	100·00 „

nic oxide, of course, renders these gases highly poisonous, and fatal acci-
asionally happen from this cause.
gh the bulk of the nitrogen present in the air escapes unchanged from the
t is not improbable that a portion of it contributes to the formation of the
f potassium (KC_2N), which is produced in the lower part of the furnace,
ium being furnished by the ashes of the fuel.

ot-blast.—On considering the enormous quantity of air which
rough the blast furnace, it will be seen that it occasions the loss of
erable amount of heat. In order to economise the fuel, *hot-blast*
are fed with air of which the temperature is raised to about
by passing it through heated iron pipes before allowing it to
blast furnace. The higher temperature which is thus attained
the use of uncoked coal, which would not have given enough heat
-blast furnace, and the same quantity of ore may be smelted with
half the coal formerly employed. It appears, however, that the
iron is inferior in quality to that obtained from the same ore in a
t furnace, and this is generally explained by referring to the larger
of sulphur contained in the raw coal; to the circumstance, that the
being exposed to a much higher temperature in the hot-blast
more liable to receive and retain a larger amount of foreign sub-

stances; and (most important of all) to the custom of extracting i hot-blast furnace from slags obtained in the subsequent processes iron-manufacture, which could not be smelted in a cold-blast f These slags always contain sulphur and phosphorus, and therefore y inferior quality of iron. Hence the distinction commonly drawn b *mine-iron* extracted from the ore without admixture of slags, and *iron* in the preparation of which slag or cinder has been employed.

The *slag from the blast furnace* is essentially a glass compos double silicate of alumina and lime, the composition of which varie according to the nature of the earthy matters in the ore, and th position of the flux. Its colour is generally opaque white, streak blue, green, or brown.

The nature of the flux employed must, of course, be modified ac to the composition of the earthy substances (or *gangue*) present in t Where this consists of clay (silicate of alumina) the addition c (which is sometimes added in the form of limestone and someti quick-lime) will provide for the formation of the double silicate of a and lime. But if the iron-ore happened already to contain limest addition of clay would be necessary, or if quartz were present, co of silica only, both lime and alumina (in the form of clay) will be sary as a flux. It is sometimes found economical to employ a mix ores containing different kinds of gangue, so that one may serve a to the other. If a proper proportion of lime were not added, a po the oxide of iron would combine with the silica and be carried off slag, but if too large a quantity of lime be employed, it will dimin fusibility of the slag, and prevent the complete separation of the iv the earthy matter. The most easily fusible slag which can be for the action of lime upon clay has the composition $6CaO . Al_2O_3 . 9Si($ in English furnaces, where coal and coke are employed, it is found sary to employ a larger proportion of lime to convert the sulphur fuel into sulphide of calcium, so that the slag commonly has a c tion more nearly represented by the formula, $12CaO . 2Al_2O_3$ which would express a compound of 6 eqs. of normal silicate of lir 1 eq. of normal silicate of alumina, $6(2CaO . SiO_2) , 2Al_2O_3 . 3SiO_2$ acid being considered a bibasic acid.

Since iron, manganese, and magnesium are commonly found oc the place of a portion of the calcium, a more general formula slag from English blast furnaces would be—

$$6(2[CaFeMnMg]O . SiO_2) , 2Al_2O_3 . 3SiO_2 .$$

A fair impression of the ordinary composition of the slag fro furnaces is conveyed by the following table :—

Slag from Blast Furnace.

Silica,	43·07
Alumina,	14·85
Lime,	28·92
Magnesia,	5·87
Oxide of iron (FeO)	2·53
Oxide of manganese (MnO),	1·87
Potash,	1·84
Sulphide of calcium,	1·90
Phosphoric acid,	trace
	100·85

slags are sometimes run from the blast furnace into iron moulds, h they are cast into blocks for rough building purposes. The of a considerable proportion of potash has led to experiments eir employment as a manure, for which purpose they have been ut, when liquid, into a finely divided frothy condition fit for grind- applying to the soil.

CAST-IRON is, essentially, composed of iron with from 2 to 5 per carbon, but always contains other substances derived either from or from the fuel employed in smelting it. On taking into con- n the energetic deoxidising action in the blast furnace, it is not ng that portions of the various oxygen compounds exposed to it part with their oxygen, and that the elements thus liberated ind their way into the cast-iron. In this way the silicic acid is , and its silicon is found in cast-iron in quantity sometimes amount- 3 or 4 per cent. Sulphur and phosphorus are also generally pre- cast-iron, but in very much smaller quantity; their presence hes its tenacity, and the smelter endeavours to exclude them as far ble, though a small quantity of phosphorus appears to be rather geous for some castings, since it augments the fusibility and of the cast-iron. The sulphur is chiefly derived from the coal or ployed in smelting, and for this reason charcoal would be pre- to any other fuel if it could be obtained at a sufficiently cheap The iron-works of America and those of the European continent great advantage in this respect over those of England. The rus is obtained from the phosphoric acid existing in the ore or in . Manganese, amounting to 1 or 2 per cent., is often met with in n, having been reduced from the oxide of manganese, which is y found in iron ores. Other metals, such as chromium, cobalt, also occasionally present, though in so small quantities as to be portance in practice.

ollowing table exhibits the largest and smallest proportions of the elements determined in the analysis of upwards of a hundred ns of cast-iron :—

*Composition of Cast-iron.**

	Max.	Min.	
Carbon,	4·81	1·04	per cent.
Silicon,	4·77	0·08	,,
Sulphur,	1·06	0·00	,,
Phosphorus,	1·87	trace	,,
Manganese,	6·08	trace	,,
Iron,	...	...	

der to understand the differences observed in the several varieties ron, it is necessary to consider the peculiar relations between iron bon. Iron fused in contact with carbon is capable of combining arly 6 per cent. of that element, to form a white, brilliant, and compound which may be represented pretty nearly as composed . Under certain circumstances, as this compound of iron and cools, a portion of the carbon separates from the iron, and remains nated throughout the mass in the form of minute crystalline par- ery much resembling natural graphite. If a broken piece of iron ing these scales be examined, the fracture will be found to exhibit

* *Compiled from* "Percy on Iron and Steel."

a more or less dark grey colour, due to the presence of the uncomb carbon, and for this reason a cast-iron in which a portion of the ca has thus separated is commonly spoken of as *grey iron*, whilst th which the whole of the carbon has remained in combination with metal exhibits a white fracture, and is termed *white iron* or *bright* Intermediate between these is the variety known as *mottled iron*, w has the appearance of a mixture of the grey and white varieties.

The different condition of the carbon in the two varieties of cast-ir rendered apparent when the metal is dissolved in diluted sulphuri hydrochloric acid, for any carbon which exists in the uncombined will then be left, whilst that which had been in combination with iron passes off in the form of peculiar compounds of carbon and hydr which impart the disagreeable odour perceived in the gas evolved the metal is dissolved in an acid.

The properties of these two varieties of cast-iron are widely diffe grey iron being so soft that it may be turned in a lathe, whilst the iron is extremely hard and brittle. Again, although white iron fu a lower temperature than grey-iron, the latter is far more liquid fused, and is therefore much better fitted for casting.

Although the presence of uncombined carbon is the chief point distinguishes grey from white iron, other differences are commonly ob in the composition of the two varieties. Thus white iron usually co less silicon than grey iron, but a larger proportion of sulphur. iron also usually contains a much larger quantity of manganese.

The difference in the composition of these three varieties of cast-i shown in the following table :—

	Grey.	Mottled.	White.
Iron	90.24	89·31	89·86
Combined carbon . .	1·02	1·79	2·46
Graphite	2·64	1·11	0·87
Silicon	3 06	2·17	1·12
Sulphur	1·14	1·48	2·52
Phosphorus	0·93	1·17	0·91
Manganese	0·83	1·60	2·72
	99·86	98·68	100·46

As might be expected, it is not easy to tell where a cast-iron co be grey and begins to be mottled, or where the mottled iron end white iron begins. There are, in fact, eight varieties of cast-iron i merce distinguished by the numbers one to eight, of which No. 1 i grey, and contains the largest proportion of graphite, which diminis the succeeding numbers up to No. 8, which is the whitest iron, the mediate numbers being more or less mottled.

The particular variety of cast-iron produced is to some extent the control of the smelter, a furnace in good order appearing usu yield grey iron, whilst a defective furnace, or one supplied with too a proportion of fuel, will commonly give a white iron. But the sometimes varies considerably at different levels in the *crucible* furnace, so that pigs of different degrees of greyness are obtained same tapping.

Mottled cast-iron surpasses both the other varieties in tenacit

herefore preferred for such purposes as casting ordnance, where this ity is particularly desirable.

he dark grey iron used for casting, known as *foundry-iron*, is produced upplying the blast furnace with a larger proportion of fuel than is oyed in making the lighter *forge-iron* destined for conversion into ght-iron. The extra consumption of fuel, of course, renders the dry-iron more expensive. When a furnace is worked with a low ge of fuel to produce a white iron, a larger quantity of iron is lost he slag, sometimes amounting to 5 per cent. of the metal, whilst average loss in producing grey iron does not exceed 2 per cent. containing a large proportion of manganese are generally found to a white iron.

hen grey iron is melted, the particles of graphite to which its grey ur is due are dissolved by the liquid iron, and if it be poured into ld iron mould so as to solidify it as rapidly as possible, the external ion of the casting will present much of the hardness and appear- of white iron, the sudden cooling having prevented the separation he graphite. This affords the explanation of the process of *chill- ing*, by which shot, &c., made of the soft fusible grey iron, are made equire externally a hardness approaching that of steel.

he *specific gravity* of cast-iron varies between 6·92 and 7·53, and its *ng point* is somewhat below 3000° F.

Conversion of Cast-Iron into Bar or Wrought Iron.

114. In order to convert cast-iron into bar-iron, it is necessary to reduce s far as possible to the condition of pure iron by removing the carbon, con, and other substances associated with it. This purification is cted upon the principle, that when cast-iron is strongly heated in con- t with oxide of iron, its carbon is evolved in the form of carbonic oxide, ilst the silicon, also combining with the oxygen from a part of the de of iron, is con- ted into silicic acid, ich unites with an- er portion of oxide form a fusible slag ily separated from the tal.

he most important the processes em- yed for the conver- of pig-iron into bar- , is that known as *puddling* process, this is sometimes eded by the process *efining*, which will efore be first de- bed.

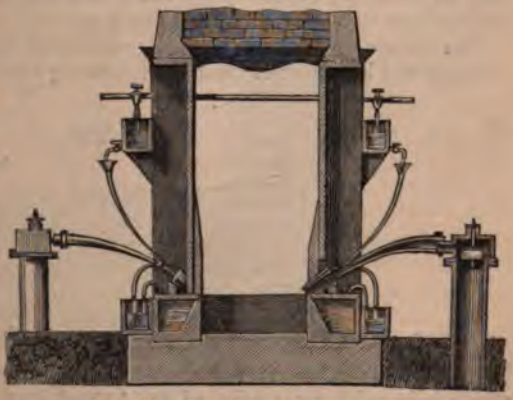


Fig. 230.—Hearth for refining pig-iron.

efining of cast-iron.—This process consists essentially in exposing the al, in a fused state, to the action of a blast of air. The *refinery* (figs. *231) is a rectangular trough* with double walls of cast-iron, between

which cold water is kept circulating to prevent their fusion. This trough is about 3½ feet long by 2½ wide, and usually lined with fire-clay; on each side of it are arranged three tuyère pipes for the supply of air, inclined at an angle of 25° to 30° to the bottom of the furnace, which is fed with coke, unless the very best iron is required, as for the manufacture of tin-plate, when charcoal is generally used in the refinery.

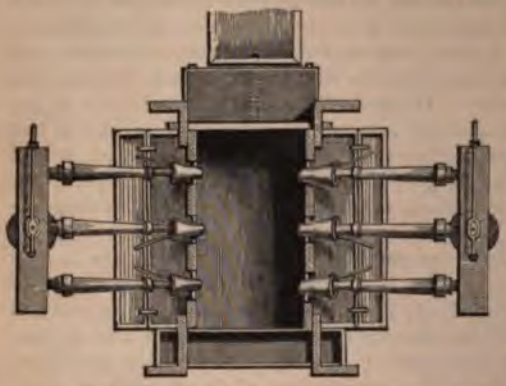


Fig. 231.—Hearth for refining pig-iron.

This furnace having been filled to a certain height with fuel, five or six pigs of iron (from 20 to 30 cwt.) are arranged symmetrically upon it, a blast of air being forced in through the tuyères, under a pressure of about 3 lbs. upon the inch. In about a quarter of an hour the metal begins to fuse gradually, and to trickle down through the fuel to the bottom of the refinery, a portion of the iron being converted into oxide in its descent, by the air issuing from the tuyère pipes. When the whole of the metal has been fused, the air is still allowed to play for some time upon its surface, when the fused metal appears to boil in consequence of the escape of bubbles of carbonic oxide.

After about two hours the tap hole is opened, and the molten metal run out into a flat mould; when it begins to solidify, water is thrown upon its surface in order to chill it and render it brittle. The plate of *refined iron* thus obtained is usually about 2 inches thick. The slag (or *finery cinder*) is generally received in a separate mould; its composition may be generally expressed by the formula $2FeO.SiO_2$, the silicic acid having been derived from the silicon contained in the cast-iron.

The change effected in the composition of the iron by the process of refining will be apparent from the following table:—

Refined Iron.

Iron,	95·14
Carbon,	3·07
Silicon,	0·63
Sulphur,	0·16
Phosphorus,	0·73
Manganese,	trace
Slag,	0·44
	100·17

The carbon, therefore, is not nearly so much diminished as the silicon, which is in some cases reduced to $\frac{1}{10}$th of its former proportion by the refining process. Half of the sulphur is also sometimes removed, being found in the slag as sulphide of iron. The phosphorus is not removed to the same extent in the refining process, though some of it is converted into *phosphoric* acid, which may be found in the finery cinder.

further purification of the metal could not be effected in the since the fusibility of the iron is so greatly diminished as it nes to a pure state, that it could not be retained in a fluid condi- the temperature attainable in this furnace, and a more spacious s required upon which the pasty metal may be kneaded into close with the oxide of iron which is to complete the oxidation and on of the carbon. For this reason the metal is transferred to the g furnace.

puddling process is carried out in a reverberatory furnace (figs. 232, nnected with a tall chimney provided with a damper, so as to admit y perfect regulation of the draught. A bridge of fire-brick between

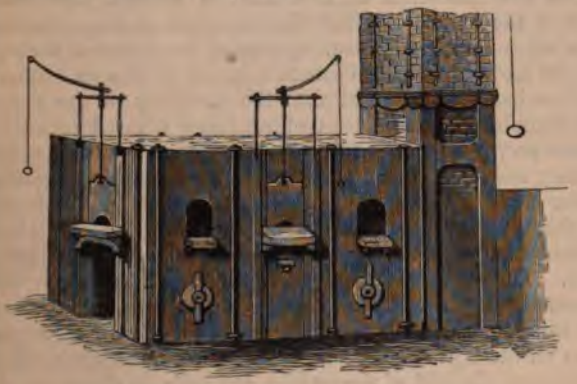


Fig. 232.—Puddling furnace.

e and the hearth prevents the contact of the coal with the iron to led. The hearth is composed either of fire-brick or of cast-iron overed with a layer of a very infusible slag, and cooled by a free

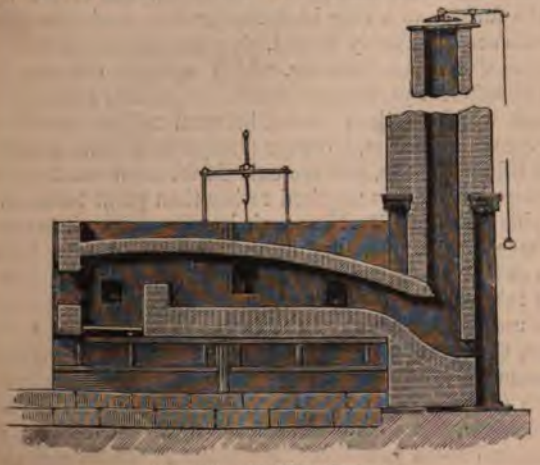


Fig. 233.—Puddling furnace.

on of air beneath them. This hearth is about 6 feet in length, by *the widest part near the grate*, and 2 feet at the opposite end;

it is slightly inclined towards the end farthest from the grate, and finishes in a very considerable slope, at the lowest point of which is the *floss-hole* for the removal of the slag. Since the metal is to attain a very high temperature in this furnace (estimated at 3000° F.), it is usually covered with an iron casing, so as to prevent any entrance of cold air through chinks in the brick work.

About 5 cwt. of the fine metal is broken up and heaped upon the hearth of this furnace, together with about 1 cwt. of iron scales (black oxide of iron, Fe_3O_4), and of *hammer-slag* (basic silicate of iron, obtained in subsequent operations), which are added in order to assist in oxidising the impurities. When the metal has fused, the mass is well stirred or puddled, so that the oxide of iron may be brought into contact with every part of the metal, to effect the oxidation of the impurities. The metal now appears to boil, in consequence of the escape of carbonic oxide, and in about an hour from the commencement of the puddling, so much of the carbon has been removed that the fusibility of the metal is considerably diminished, and instead of retaining a fused condition at the temperature prevailing in the furnace, it assumes a granular, *sandy*, or *dry* state, spongy masses of pure iron separating or *coming to nature* in the fused mass. The puddling of the iron is continued until the whole has assumed this granular appearance, when the evolution of carbonic oxide ceases almost entirely, showing that the removal of the carbon is nearly completed. The damper is now gradually raised, so as to increase the temperature and soften the particles of iron, in order that they may be collected into a mass; and the more easily to effect this, a part of the slag is run off through the floss-hole. The workman then collects some of the iron upon the end of the paddle, and rolls it about on the hearth until he has collected a sort of rough ball of iron, weighing about half-a-hundred weight. When all the iron has been collected into balls in this way, they are placed in the hottest part of the furnace, and pressed occasionally with the paddle, so as to squeeze out a portion of the slag with which their interstices are filled. The doors are then closed to raise the interior of the furnace to a very high temperature, and after a short time, when the balls are sufficiently heated, they are removed from the furnace, and placed under a steam hammer, which squeezes out the liquid slag, and forces the softened particles of iron to cohere into a continuous oblong mass or *bloom*, which is then passed between rollers by which it is extended into bars. These bars, however (*Rough* or *Puddled*, or *No.* 1 *Bar*), are always hard and brittle, and are only fit for such constructions as railway bars, where hardness is required rather than great tenacity. In order to improve this latter quality, the rough bars are cut up into short lengths, which are made into bundles, and after being raised to a high temperature in the *mill-furnace*, are passed through rollers, which weld the several bars into one compound bar, to be subsequently passed through other rollers until it has acquired the desired dimensions. By thus *fagotting* the bars, their texture is rendered far more uniform, and they are made to assume a fibrous structure, which appears greatly to increase their strength (*Merchant Bar*, or *No.* 2 *Bar*). To obtain the best, or *No.* 3 *Bar*, or *wire-iron*, these bars are doubled upon themselves, raised to a welding heat, and again passed between rollers. These repeated rollings have the effect of thoroughly squeezing out the slag which is mechanically entangled among the particles of iron in the rough bars, and would produce flaws if allowed to remain in the metal. A slight improvement

appears also to be effected in the chemical composition of the iron during the rolling, some of the carbon, silicon, phosphorus, and sulphur, still retained by the puddled iron, becoming oxidised, and passing away as carbonic oxide and slag.

The following table exhibits the change in chemical composition which takes place in pig-iron when puddled (without previous refining) and rolled into wire-iron :—

Effect of Puddling and Forging on Cast-Iron.

In 100 parts.	Carbon.	Silicon.	Sulphur.	Phosphorus.
Grey pig-iron, . .	2·275	2·720	0·301	0·645
Puddled bar, . . .	0·296	0·120	0·134	0·139
Wire-iron, ...	0·111	0·088	0·094	0·117

About 90 parts of bar-iron are obtained from 100 of pig-iron by the puddling process, the difference representing the carbon which has passed off as carbonic oxide, and the silicon, sulphur, phosphorus, and iron, which have been removed in the slag or *tap-cinder*, this being essentially a silicate of protoxide and sesquioxide of iron, varying much in composition according to the character of the iron employed for puddling, and the proportions of iron-scale and hammer-slag introduced into the furnace. Of course, also, the material of which the hearth is composed will influence the composition of the slag. The following table affords an illustration of its composition :—

Tap-Cinder from Puddling Furnace.

Protoxide of iron (FeO), . . .	57·67
Peroxide of iron (Fe_2O_3), . .	13·53
Silicic acid, ...	8·32
Phosphoric acid, ...	7·29
Sulphide of iron, ...	7·07
Lime, ...	4·70
Oxide of manganese, . . .	0·78
Magnesia, ...	0·26
	99·62

The lime in the above cinder was probably derived from the hearth of the furnace, which is sometimes lined with that material to assist in removing the sulphur.

When pig-iron is puddled without undergoing the refining process, it becomes much more liquid than refined iron, and the process is sometimes described as the *boiling process*, whilst refined iron undergoes *dry puddling*.

It will be observed that this process of puddling is attended with some important disadvantages ; it involves a great expenditure of manual labour, and of a most exhausting kind ; the very high temperature to which the puddler is exposed renders him liable to lung disease, and cataract is not uncommonly caused by the intense light from the glowing iron ; the wear and tear of the puddling furnace is very considerable, and since it receives only ten or eleven charges of about five cwts. each in the course of twenty-four hours, it is necessary to work five or six puddling furnaces at once, in order to convert into bar-iron the whole of the cast-

iron turned out from a single blast furnace. These considerations have led to several attempts to improve the puddling process by employing revolving furnaces and other mechanical arrangements to supersede the heavy manual labour, and even to dispense with it altogether by forcing the air into the molten iron. The most generally known of the processes devised for this purpose is that of Bessemer, which consists in running the melted cast-iron into a huge crucible, and forcing air up through it under considerable pressure, thus combining the purifying influence of the blast of air in the refinery with the mechanical agitation effected in the puddling furnace. Bessemer's *converting vessel* (fig. 234) is a large, nearly cylindrical crucible of wrought iron, lined with fire-clay, having apertures (A) at the bottom, through which air is blown at a pressure of fifteen or twenty pounds upon the inch. This vessel is sometimes large enough to receive ten tons of cast-iron for a charge. The metal having been melted in a separate furnace, is run into the converting vessel, the blast being already turned on so that the liquid iron may not run into the air tubes. The iron burns vividly in the current of air, and the oxide of iron produced is diffused in a melted state through the mass of metal by the rapid current of air. This oxide of iron acts upon the silicon and carbon in the cast-iron, converting the latter into carbonic oxide, which burns with flame at the mouth of the converter, and the former into silicic acid, which enters into the slag, and is carried up as a froth to the surface of the liquid iron. The blast of air is continued for about twenty minutes, when the disappearance of the flame of carbonic oxide indicates the completion of the process; but the remaining purified iron is not pasty, as in the puddling furnace, being retained in a perfectly liquid condition by the high temperature resulting from the combustion of part of the iron, so that the metal may be run out into moulds by tilting the converting vessel. In this way about 85 parts of bar-iron are obtained from 100 of pig-iron.

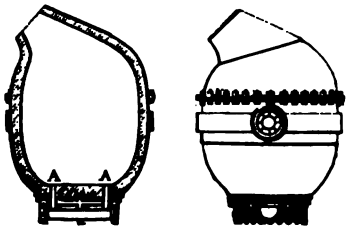


Fig. 234.—Bessemer's converting vessel.

Although so great an economy of time and labour would result from the application of Bessemer's process, it has not superseded the puddling process, because it does not remove the sulphur and phosphorus from the pig-iron, so that only the best varieties of that material, extracted from hæmatite or magnetic ore, yield a bar-iron of good quality when purified in this way. Its application to the manufacture of steel will be noticed hereafter. The effect of the Bessemer process upon a particular specimen of pig-iron is shown in the table.

In 100 parts of Pig-iron.	Before.	After.
Carbon, ...	3·309	0·218
Silicon, ...	0·595	none
Sulphur, ...	0·485	0·402
Phosphorus, ...	1·012	1·102

Composition of bar-iron.—Even the best bar-iron contains from 0·1 to

per cent. of carbon, together with minute proportions of silicon, sulur, and phosphorus. Perfectly pure iron is inferior in hardness and acity to that which contains a small proportion of carbon.

Bar-iron is liable to two important defects, which are technically known *cold-shortness* and *red-shortness*. Cold-short iron is brittle at ordinary peratures, and appears to owe this to the presence of phosphorus, which element 0·5 per cent. is sufficient materially to diminish the acity of the iron. When the iron is liable to brittleness at a red heat, s termed red-short iron, and a very little sulphur is sufficient to affect quality of the iron in this respect.

There is much difference of opinion as to the true causes of the variain the strength of wrought-iron, and this is not surprising when reflect upon the number of circumstances which may be reasonably pected to exert some influence upon it. Not only the proportions of bon, silicon, sulphur, phosphorus, and manganese may be supposed to ect the quality of the iron, but the state of combination in which these ments exist in the mass is not unlikely to cause a difference. It also pears certain that the mechanical structure, dependent upon the arrangent of the particles composing the mass of metal, has at least as much fluence upon the tenacity of the iron as its chemical composition.

The best bar-iron, if broken slowly, always exhibits a fibrous structure, e particles of iron being arranged in parallel lines. This appears to conibute greatly to the strength of the iron, for when it is wanting, and the r is composed of a confused mass of crystals, it is weaker in proportion the size of the crystals. The presence of phosphorus is said to favour e formation of large crystals, and hence to produce cold-shortness. There some reason to believe that the fibrous is sometimes exchanged for the ystalline texture under the influence of frequent vibrations, as in the se of railway axles, girders of suspension-bridges, &c.

Considering the difficult fusibility of bar-iron, it is fortunate that it ssesses the property of being *welded*, that is, of being united by hamering when softened by heat. It is customary first to sprinkle the eated bars with sand or clay in order to convert the superficial oxide of on into a liquid silicate, which will be forced out from between them by ammering, leaving the clean metallic surfaces to adhere. *Burnt iron* oes not weld, and is largely crystalline in structure.

Manufacture of Steel.

215. Steel differs from bar-iron in possessing the property of becoming ery hard and brittle when heated to redness and then suddenly cooled y being plunged into water. Perfectly pure iron, obtained by the electrotype process, is not hardened by sudden cooling; but all bar-iron hich contains carbon does exhibit this property in a greater or less egree according to the proportion of carbon present. It does not become cidedly steely, however, until the carbon amounts to 0·5 per cent. The st steel contains about 1·5 per cent. of carbon, and when the proportion aches 1·7 per cent. it begins to assume the properties of cast-iron. Barn may, therefore, be converted into steel by the addition of about 1·5 r cent. of carbon, and, conversely, cast-iron is converted into steel when e quantity of carbon contained in it is reduced to about 1·5 per cent. *ere are thus two processes by* which steel may be produced; but that

which is employed almost exclusively in this country consists in combining bar-iron with the requisite amount of carbon by what is technically known as *cementation*, the bars being imbedded in charcoal and exposed for several days to a high temperature.

The operation is effected in large chests of fire-brick or stone, about 10 or 12 feet long by 3 feet wide and 3 feet deep.

Fig. 235.—Furnace for converting bar-iron into steel.

Two of these chests are built into a dome-shaped furnace (*converting furnace*, fig. 235), so that the flame may circulate round them, and the furnace is surrounded with a conical jacket of brick-work in order to allow a steady temperature to be maintained in it for some days. The charcoal is ground so as to pass through a sieve of $\frac{1}{4}$ inch mesh, and spread in an even layer upon the bottom of the chests. Upon this the bars of iron, which must be of the best quality, are laid in regular order, a small interval being left between them, which is afterwards filled in with the charcoal powder, with a layer of which the bars are now covered; over this more bars are laid, then another layer of charcoal, and so on until the chest is filled. Each chest holds 5 or 6 tons of bars. One of the bars is allowed to project through an opening in the end of the chest, so that the workmen may withdraw it from time to time and judge of the progress of the operation. The whole is covered in with a layer of about 6 inches of damp clay or sand.

The fire is carefully and gradually lighted, lest the chests should be split by too sudden application of heat, and the temperature is eventually raised to about the fusing point of copper (2000° F.), at which it is maintained for a period varying with the quality of steel which it is desired to obtain. Six or eight days suffice to produce steel of moderate hardness; but the process is continued for three or four days longer if very hard steel be required. The fire is gradually extinguished, so that the chests are about ten days in cooling down.

On opening the chests, the bars are found to have suffered a remarkable change both in their external appearance and internal structure. They are covered with large blisters, obviously produced by some gaseous substance raising the softened surface of the metal in its attempt to escape. It is conjectured either that the small quantity of sulphur present in the bar-iron is converted into bisulphide of carbon during the cementation process, and that the vapour of this substance swells the softened metal

to bubbles as it passes off; or that the blisters are caused by carbonic ide produced by the action of the carbon upon particles of slag acci- ntally present in the bar. On breaking the bars across, the fracture is nd to have a finely granular structure, instead of the fibrous appearance hibited by bar-iron. Chemical analysis shows that the iron has com- ned with about 1·5 per cent. of carbon, and the most remarkable part the result is that this carbon is not only found in the external layer of n, which has been in direct contact with the heated charcoal, but is so present in the very centre of the bar. It is this transmission of the id carbon through the solid mass of iron which is implied by the term *mentation*. The chemistry of the process probably consists in the forma- on of carbonic oxide from the small quantity of atmospheric oxygen in e chest, and the removal of one-half of the carbon from this carbonic ide, by the iron, which it converts into steel, leaving carbonic acid $CO - C = CO_2$) to be reconverted into carbonic oxide by taking up ore carbon from the charcoal ($CO_2 + C = CO$), which it transfers again the iron. Experiment has recently shown that soft iron is capable of sorbing, mechanically, 4·15 volumes of carbonic oxide at a low red heat, that the action of the gas upon the metal may occur throughout the ubstance of the bar. The carbonic oxide is retained unaltered by the on, after cooling, unless the bar is raised to the temperature required for he production of steel.

The *blistered steel* obtained by this process is, as would be expected, far from uniform either in composition or in texture; some portions of the bar contain more carbon than others, and the interior contains nume- rous cavities. In order to improve its quality, it is subjected to a process of fagotting similar to that mentioned in the case of bar-iron; the bars of blistered steel, being cut into short lengths, are made up into bundles, which are raised to a welding heat, and placed under a tilt-hammer weighing about 2 cwt., which strikes two or three hundred blows in a minute; in this way, the several bars are consolidated into one compound bar, which is then extended under the hammer till of the required dimensions. The bars, before being hammered, are sprinkled with sand, which combines with the oxide of iron upon the surface, and forms a vitreous layer which protects the bar from further oxidation. The steel which has been thus hammered is much denser and more uniform in composition; its tenacity, malleability, and ductility are greatly in- creased, and it is fitted for the manufacture of shears, files, and other tools. It is commonly known as *shear steel*. Double shear steel is obtained by breaking the tilted bars in two, and welding these into a compound bar.

The best variety of steel, however, which is perfectly homogeneous in composition, is that known as *cast steel*, to obtain which, about 30 lbs. of blistered steel are broken into fragments, and fused in a fire-clay crucible, heated in a wind-furnace, the surface of the metal being protected from oxidation by a little glass melted upon it. The fused steel is cast into ingots, several crucibles being emptied simultaneously into the same mould. Cast steel is far superior in density and hardness to shear steel, but since it is exceedingly brittle at a red heat, great care is necessary in forging it. It has been found that the addition, to 100 parts of the cast steel, of one part of a mixture of charcoal and oxide of manganese, pro- duces a very fine grained steel which admits of being cast on to a bar of *wrought-iron in the ingot-mould*, so that the tenacity of the latter may

compensate for the brittleness of the steel when the compound bar is forged, the wrought-iron forming the back of the implement, and the steel its cutting edge.

This addition of manganese to the cast steel (Heath's patent) has effected a great reduction in its cost, allowing the use of blister steel made from British bar-iron, whereas, before its introduction, only the expensive iron of Swedish or Russian make could be employed.

After the steel has been forged into the shape of any implement, it is hardened by being heated to redness, and suddenly chilled in cold water or oil, or mercury. It is thus rendered nearly as hard as diamond, at the same time increasing slightly in volume (sp. gr. of cast steel 7·93, after hardening, 7·66). The chemical difference between hard and soft steel appears to be of the same kind as that between grey and white cast-iron (p. 307), the great proportion of the carbon in hard steel being in combination with the metal, while in soft steel the greater part seems to be in intimate mechanical admixture with the iron, for it is left undissolved on treating the steel with an acid. If the hardened steel be heated to redness, and allowed to cool slowly, it is again converted into soft steel, but by heating it to a temperature short of a red heat, its hardness may be proportionally reduced. This is taken advantage of in annealing the steel or "letting it down" to the proper temper. The very hardest steel is almost as brittle as glass, and totally unfit for any ordinary use, but by heating it to a given temperature and allowing it to cool, its elasticity may be increased to the desired extent, without reducing its hardness below that required for the implement in hand. On heating a steel blade gradually over a flame, it will acquire a light yellow colour when its temperature reaches 430° F., from the formation of a thin film of oxide; as the temperature rises, the thickness of the film increases, and at 470° a decided yellow colour is seen, which assumes a brown shade at 490°, becomes purple at 520°, and blue at 550°. At a still higher temperature the film of oxide becomes so thick as to be black and opaque. Steel which has been heated to 430°, and allowed to cool slowly, is said to be *tempered to the yellow*, and is hard enough to take a very fine cutting edge, whilst, if *tempered to the blue*, at 550°, it is too soft to take a very keen edge, but has a very high degree of elasticity. The following table indicates the tempering heats for various implements:—

Tempering of Steel.

Temperature, F.	Colour.	Implements thus tempered.
430° to 450°.	Straw-yellow.	Razors, lancets.
470°	Yellow.	Pen-knives.
490°	Brown-yellow.	Large shears for cutting metal.
510°	Brown-purple.	Clasp-knives.
520°	Purple.	Table-knives.
530° to 570°.	Blue.	Watch-springs, sword-blades.

If a knife blade be heated to redness, its *temper is spoilt*, for it is converted into soft steel.

In general, the steel implements are ground after being tempered, so that they are not seen of the colours mentioned above, except in the case of watch-springs.

l blade may be easily distinguished from iron by placing a drop
d nitric acid upon it, when a dark stain is produced upon the
m the separation of the carbon.
small instruments, such as keys, gun-locks, &c., which are ex-
considerable wear and tear by friction, and require the external
of steel without its brittleness, are forged from bar-iron, and
l externally into steel by the process of *case-hardening*, which
n heating them in contact with some substance containing carbon
bone-dust, yellow prussiate of potash, &c.) A process which is
se of this is adopted in order to increase the tenacity of stirrups,
similar articles made of cast-iron; by heating them for some
contact with oxide of iron or manganese, their carbon and silicon
ved in the forms of carbonic oxide and silicic acid, and they be-
verted into *malleable cast-iron.*

pinion that steel owes its properties entirely to the presence of
not universally entertained. Some chemists believe that nitrogen
analogous element) is an indispensable constituent, but the pro-
f nitrogen found in steel is too minute to warrant this supposi-
tanium is alleged by some authorities to have an important
upon the quality of steel, but this also appears to be a doubtful
Bar-iron may be converted into steel by being kept at a high
ure in an atmosphere of coal-gas, from which it abstracts carbon.

er steel was originally produced by arresting the purification of
in Bessemer's process (page 314), as soon as the carbon had dimi-
about 1·5 per cent., when the steel was poured out in the fused
, in the form of cast steel. A steel of better quality, however,
obtained by continuing the purification until liquid bar-iron
n the converter, and introducing the proper proportion of carbon
m of a peculiar description of white cast-iron known as *Spiegel-*
rror iron), which crystallises in lustrous tabular crystals, and
large proportions of carbon and manganese, being obtained by
spathic iron ore rich in manganese, with charcoal as fuel. The
sen is added, in a melted state, to the Bessemer iron before pour-
the converter.
mposition of a sample of *Spiegel-eisen* smelted from a spathic ore,
ar Müsen in Prussia, is here given :—

Spiegel-eisen.

Iron, . . .	82·86
Manganese, . .	10·71
Silicon, . . .	1·00
Carbon, . . .	4·32
	98·89

eneous iron, as it is called, is really a *mild* steel containing a low
e of carbon, and obtained by fusing the best Swedish bar-iron
bonaceous matters. It is remarkable for its malleability and
s, and, having undergone complete fusion, it is more likely to be
eous in composition and structure than wrought-iron produced
ing.
s steel is manufactured by melting bar-iron with fuel free from
nd phosphorus, so as to obtain a very pure cast-iron, which is

then partly decarbonised by a process similar to Bessemer's. Th
tion of manganese improves its quality.

Puddled steel is obtained by arresting the puddling process at an
stage than usual, so as to leave a proportion of carbon varying fr
to 1·0 per cent.

Natural steel or *German steel* results in a similar way, from the
plete purification of cast-iron in the refinery. The presence of man
in the iron is favourable to its production.

Krupp's cast steel, manufactured at Essen near Cologne, and em
for ordnance, shells, &c., is a puddled steel made from hæmatite and
ore, smelted with coke. The iron thus obtained contains much man
which is removed in the puddling process. Krupp's steel contains
1·2 per cent of combined carbon, and is fused with a little bar-ir
casting ordnance. The fusion is effected in black lead crucibles h
30 lbs. each, of which as many as 1200 are emptied simultaneous
the mould for the largest castings. A casting of 16 tons requires
400 men, who act together in well-disciplined gangs, so that the
of molten metal shall flow continuously along the gutters into the
Such large castings must be allowed to cool very gradually, so th
are kept surrounded with hot cinders, sometimes for two or three n
till required for forging.

216. *Direct extraction of wrought-iron from the ore.*—Where ve
and pure ores of iron, such as hæmatite and magnetic iron ore, are
able, and fuel is abundant, the metal is sometimes extracted withou

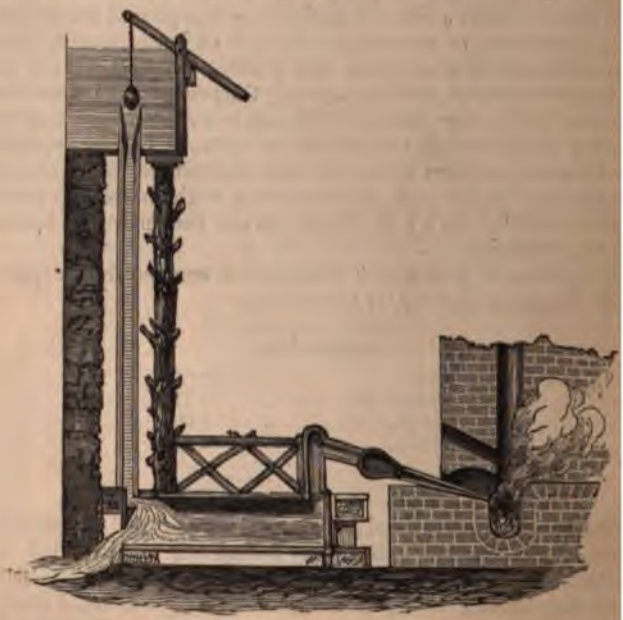


Fig. 236.—Catalan forge for smelting iron ores.

verted into cast-iron. It is probable that the iron of antiqu
ted in this way, for it is doubtful whether cast-iron was kn

ancients, and the slag left from old iron-works does not indicate the of any flux. Some works of this description are still in operation in Pyrenees, where the *Catalan process* is employed. The crucible is ed at the sides with thick iron plates, and at the bottom with a refrac- y stone. A quantity of red-hot charcoal is thrown into it, and the space ve this is temporarily divided into two compartments by a shovel. e compartment nearest to the pipe through which the blast enters is rged with charcoal, and the other compartment with the calcined ore small pieces. The shovel is then withdrawn, and a gradually increasing rent of air supplied, fresh ore and fuel being added as they sink down. e part of the oxide of iron is reduced to the metallic state by the onic oxide, and the rest combines with the silica present in the ore to a slag. After about five hours the spongy masses of bar-iron are ected into a ball upon the end of an iron rod, and hammered into a pact mass like the metal obtained in the puddling furnace. The wing machine employed in the Pyrenees is one in which the fall of er from a cistern down a long wooden pipe, sucks in, through lateral rtures, a supply of air which it carries down with it into a box, from ich the pressure of the column of water projects it with some force ough the blast-pipe, the water escaping from the box through another rture.

In the North American *bloomery forges* a modernised form of the same ocess is adopted.

The wrought-iron produced by this process always contains a larger roportion of carbon than puddled iron, and is therefore somewhat steely character.

217. *Extraction of iron on the small scale.*—In the laboratory, iron may be extracted om hæmatite in the following manner:—A fire-clay crucible (A, fig. 237), about 3 ches high, is filled with damp charcoal powder, rammed down in successive layers; smooth conical cavity is scooped in the harcoal, and a mixture of 100 grs. red hæ- atite, 25 grs. chalk, and 25 grs. pipe-clay, s introduced into it; the mixture is covered with a layer of charcoal, and a lid placed on he crucible, which is heated in a Sefström last furnace,* fed with coke in small pieces, or about half an hour. On breaking the old crucible, a button of cast-iron will be btained. Chemically pure iron may be repared by fusing the best wire-iron with bout one-fifth of its weight of pure peroxide f iron, to oxidise the carbon and silicon hich it contains. Some powdered green glass, perfectly free from lead, must be mployed as a flux, and the crucible (with its cover well cemented on with fire-clay) xposed for an hour to a very high temperature. A silvery button of pure iron will hen be obtained.

Fig. 237.—Sefström furnace.

218. *Chemical properties of iron.*—In its ordinary condition, iron is unaffected by perfectly dry air, but in the presence of moisture it is gradually converted into hydrated sesquioxide of iron ($2Fe_2O_3 . 3HO$), or *rust*. This conversion takes place more rapidly when carbonic acid is present, water being then decomposed, and carbonate of iron formed ($Fe + HO + CO_2 = FeO . CO_2 + H$); this is dissolved by the carbonic

* This very useful furnace, shown in section in fig. 237, consists of two iron cylinders with a space (B) between them, into which air is forced through the tube C by a double-action bellows. The inner cylinder has a fire-clay lining (D), through which four or six copper tubes (E) admit the blast into the fuel.

acid present, and the solution rapidly absorbs oxygen from the air, depositing the sesquioxide of iron in a hydrated state—

$$2(FeO.CO_2) + O = Fe_2O_3 + 2CO_2.$$

When iron nails are driven into a new oaken fence, a black streak will soon be observed descending from each nail, caused by the formation of tannate of iron (ink) by the action of the tannic acid in the wood upon the solution of carbonate of iron formed from the nails. The diffusion of *iron-mould* stains through the fibre of wet linen by contact with a nail is also caused by the formation of solution of carbonate of iron. The iron in *chalybeate* waters is also generally present in the form of carbonate dissolved in carbonic acid, and hence the rusty deposit which is formed when they are exposed to the air. Iron does not rust in water containing a free alkali, or alkaline earth, or an alkaline carbonate.

Concentrated sulphuric and nitric acids do not act upon iron at the ordinary temperature, though they dissolve it rapidly when diluted. Even when boiling, strong sulphuric acid acts upon it but slowly. When iron has been immersed in strong nitric acid (sp. gr. 1·45), it is found to be unacted upon when subsequently placed in diluted nitric acid, unless previously wiped; it is then said to have assumed the *passive state*. If iron wire be placed in nitric acid of sp. gr. 1·35, it is acted upon immediately, but if a piece of gold or platinum be made to touch it beneath the acid, the iron assumes the passive state, and the action ceases at once. A state similar to this, the cause of which has not yet been satisfactorily explained, is sometimes assumed by other metals, though in a less marked degree.

219. *Oxides of iron.*—Three compounds of iron with oxygen are known in the separate state, and one is believed to exist in certain compounds—

Protoxide of iron, or ferrous oxide,	FeO
Sesquioxide or peroxide of iron, or ferric oxide,	Fe_2O_3
Magnetic oxide, or ferroso-ferric oxide,	Fe_3O_4
Ferric acid (?),	FeO_3.

The *protoxide of iron* is little known in the separate state on account of the readiness with which it absorbs oxygen and forms sesquioxide of iron. If a little potash or ammonia be added to a solution of the green sulphate of iron ($FeO.SO_3$), a whitish precipitate of hydrated protoxide of iron is formed, which immediately absorbs oxygen, and is converted into the dingy green hydrate of the magnetic oxide; on exposing this to the air it absorbs more oxygen and becomes brown hydrated peroxide. This disposition of the hydrated protoxide to absorb oxygen is turned to advantage when a mixture of sulphate of iron with lime or potash is employed for converting blue into white indigo. The protoxide of iron is a strong base.

Peroxide or *red oxide of iron* has been already noticed among the ores of iron, and has also been referred to as occurring in commerce under the names of *colcothar*, *jeweller's rouge*, and *Venetian red*, which are obtained by the calcination of the green sulphate of iron—

$$2(FeO.SO_3) = Fe_2O_3 + SO_2 + SO_3.$$

The hydrated peroxide ($2Fe_2O_3.3HO$), obtained by decomposing a solution of perchloride of iron with an alkali, forms a brown gelatinous *precipitate*, which is easily dissolved by acids; but if it be dried at

ted to dull redness it exhibits a sudden glow, and is converted into a ification which is dissolved with great difficulty by acids, although as the same composition as the soluble form which has not been ngly heated. When the peroxide of iron is heated to whiteness it s oxygen, and is converted into magnetic oxide of iron—

$$3Fe_2O_3 = 2Fe_3O_4 + O .$$

sting as it does in all soils, sesquioxide of iron is believed to fulfil the pose of oxidising the organic matter in the soil, and converting its carbon carbonic acid, to be absorbed by the plant; the sesquioxide being thus uced to protoxide, which is oxidised by the air, and fitted to perform in the same office. The sesquioxide of iron, like alumina, is a weak e, and even exhibits some tendency to play the part of an acid towards ng bases, though not in so marked a degree as alumina.

Magnetic or *black oxide of iron* is generally regarded as a compound he protoxide with the sesquioxide of iron ($FeO . Fe_2O_3$), a view which onfirmed by the occurrence of a number of minerals having the same stalline form as the native magnetic oxide of iron, in which the iron, part of it, is displaced by other metals. Thus, *spinelle* is $MgO . Al_2O_3$; *nklinite*, $ZnO . Fe_2O_3$; chrome-iron ore, $FeO . Cr_2O_3$. The natural gnetic oxide was mentioned among the ores of iron, and this oxide has en seen to be the result of the action of air or steam upon iron at a gh temperature. The hydrated magnetic oxide of iron ($Fe_3O_4 . HO$) is tained as a black crystalline powder by mixing one equivalent of proto-lphate with one equivalent of persulphate of iron, and pouring the ixture into a slight excess of solution of ammonia, which is afterwards oiled with it. Magnetic oxide of iron, when acted upon by acids, yields ixtures of protosalts and persalts of iron, so that it is not an independent sic oxide.

Ferric acid is only known in combination with bases as *ferrates*. When iron filings re strongly heated with nitre, and the mass treated with a little water, a fine purple olution of ferrate of potash is obtained. A better method of preparing this salt onsists in suspending 1 part of freshly precipitated sesquioxide of iron in 50 parts f water, adding 30 parts of solid hydrate of potash, and saturating the mixture ith chlorine ($Fe_2O_3 + Cl_3 + 5KO = 3KCl + 2(KO . FeO_3)$; the ferrate of potash rms a black precipitate, being insoluble in the strongly alkaline solution, though dissolves in pure water to form a purple solution, which is decomposed even by lution, oxygen escaping, and hydrated peroxide of iron being precipitated; $KO . FeO_3) = 2KO + Fe_2O_3 + O_3$. A similar decomposition takes place on iling a strong solution, or on adding an acid with a view to liberate the ferric id. The ferrates of baryta, strontia, and lime are obtained as fine red precipitates hen solutions of their salts are mixed with ferrate of potash.

220. *Protosulphate of iron, copperas, green vitriol,* or *ferrous sulphate,* easily obtained by heating 1 part of iron wire with $1\frac{1}{2}$ parts of strong lphuric acid, mixed with 4 times its weight of water, until the whole of e metal is dissolved, when the solution is allowed to crystallise. Its nufacture on the large scale by the oxidation of iron pyrites has been eady referred to.

It forms fine green rhomboidal crystals, having the composition—

$$FeO . SO_3 . HO + 6Aq.$$

e colour of the crystals varies somewhat, from the occasional presence small quantities of the sulphate of sesquioxide of iron ($Fe_2O_3 . 3SO_3$). It solves very easily in twice its weight of cold water, yielding a pale green *ution. When the commercial* sulphate of iron is boiled with water, it

yields a brown muddy solution, in consequence of the decomposition of t sulphate of sesquioxide of iron contained in it, with precipitation of a ba sulphate. The sulphate of iron has a great tendency to absorb oxyg and to become converted into the sulphate of sesquioxide. Thus, t ordinary crystals when exposed to air gradually become brown, and converted into a mixture of the neutral and basic sulphates of t sesquioxide of iron—

$$10(FeO.SO_3) + O_5 = 3(Fe_2O_3.3SO_3) + 2Fe_2O_3.SO_3.$$

This disposition to absorb oxygen renders the sulphate of iron useful a reducing agent; thus, it is employed for precipitating gold in the metal state from its solutions. But its chief use is for the manufacture of i and black dyes, by its action upon vegetable infusions containing tan acid, such as that of nut-galls. This application will be more particula noticed hereafter.

Sulphate of sesquioxide of iron, or *persulphate of iron*, or *ferric sulph* is found in Chile as a white silky crystalline mineral, *coquimbite*, hav the composition, $Fe_2O_3.3SO_3 + 9Aq$.

The *phosphates* of protoxide and sesquioxide of iron are found associa in the mineral known as *vivianite* or *native Prussian blue*.

221. *Sesquichloride*, or *perchloride of iron* or *ferric chloride* (Fe_2 is obtained in beautiful dark green crystalline scales when iron wi heated in a glass tube through which a current of dry chlorine is pas the sesquichloride passing off in vapour, and condensing in the cool pa the tube. The crystals almost instantly become wet when exposed to on account of their great attraction for water. The perchloride of may be obtained in solution by dissolving iron in hydrochloric acid, converting the protochloride of iron (FeCl) thus formed into perchlorid the action of nitric and hydrochloric acids (p. 167). The solution of chloride of iron has been recommended in some cases as a disinfec being easily reduced to protochloride, and thus affording chlorin unstable organic matters in contact with it (p. 146). A solution of chloride of iron in alcohol is used in medicine under the name of *tin of iron*.

222. *Equivalent and atomic weights of iron.*—When iron is dis in hydrochloric acid, 28 parts by weight of iron combine with (35·5 parts) of chlorine, displacing 1 part of hydrogen; hence 28 equivalent weight of iron.

The specific heat of iron and its isomorphism with magnesium, zin cadmium, show that its atomic weight must be represented by doul equivalent, or 56, so that iron is a diatomic or biequivalent element

The *atomic formulæ* of the oxides and chlorides of iron would th written thus (Fe = 56)—

Ferrous oxide, FeO	Ferrous chloride, $FeCl_2$
Ferric oxide, Fe_2O_3	Ferric chloride, Fe_2Cl_6.

The molecular formula of ferric chloride has been confirmed b determination of the specific gravity of its vapour, which has been to be 165 times that of hydrogen. If, therefore, one volume (o atom) of hydrogen be represented as having a weight = 1, *two* vo *(or one molecule)* of ferric chloride vapour would weigh (165 × 2

r nearly agreeing with the sum of two atoms of iron (112) and six
f chlorine (213·0).
l be remarked that iron possesses a different atomicity accordingly
sts in ferrous or ferric compounds. Thus, in ferrous oxide ($\dot{F}eO$)
ous chloride ($\dot{F}eCl_2$), it occupies the place of two atoms of hydrogen,
iatomic; but in ferric oxide ($\dot{F}e_2O_3$) and ferric chloride ($\dot{F}e_2Cl_6$) each
iron occupies the place of three atoms of hydrogen, and is tri-
Some chemists designate the diatomic iron existing in ferrous
nds by the name *ferrosum* ($\dot{F}e''$), and the triatomic iron of the
mpounds by *ferricum* ($\dot{F}e'''$).

MANGANESE.

Manganese much resembles iron in several particulars relating both
ysical and chemical characters, and is often found in nature, asso-
n small quantities, with the compounds of that metal. The metal
s not been applied to any useful purpose.
obtained by reducing carbonate of manganese ($MnO.CO_2$) with
, at a very high temperature, when a fused mass, composed of man-
ombined with a little carbon (corresponding to cast-iron), is ob-
which is freed from carbon by a second fusion in contact with car-
f manganese.
lic manganese is darker in colour than (wrought) iron, and very
rder; it is brittle, and only feebly attracted by the magnet. It
what more easily oxidised than iron.

Oxides of manganese.—Three distinct compounds of manganese
ygen have been obtained in the separate state, and two others are
to exist in combination, but have not been satisfactorily made
he anhydrous state—

Protoxide of manganese,	MnO
Sesquioxide ,,	Mn_2O_3
Binoxide or peroxide of manganese,	MnO_2
Manganic acid (?)	MnO_3
Permanganic acid (?)	Mn_2O_7.

oxide of manganese is the chief form in which this metal is found
e, and is the source from which all other compounds of manganese
ined. Its chief mineral form is *pyrolusite*, which forms steel-grey
e crystals; but it is also found amorphous, as *psilomelane*, and in
rated state as *wad*. In commerce pyrolusite is known as black
se, or simply manganese, and is largely imported from Germany,
c., for the use of the manufacturer of bleaching-powder, the glass-
c. It is also used as a cheap source of oxygen, which it evolves
eated to redness, leaving the *red oxide of manganese*, Mn_3O_4.
oxide of manganese is an indifferent oxide, and does not combine
ids; when heated with strong sulphuric acid, it loses half its
and forms the protoxide of manganese, which is a powerful base,
bines with the sulphuric acid to form sulphate of manganese—

$$MnO_2 + HO.SO_3 = MnO.SO_3 + HO + O.$$

e natural binoxide contains peroxide of iron, some persulphate of
rmed at the same time; but if the mixture be dried and heated to
the iron-salt is decomposed, evolving sulphuric acid, and leaving

peroxide of iron; while the protoxide of manganese, being a stronger base, does not abandon its sulphuric acid; and the sulphate of manganese may be dissolved out of the mass by treatment with water. On evaporating the solution, and allowing it to cool, it deposits light pink crystals of sulphate of manganese, $MnO.SO_3.HO + 4Aq$.

This salt is employed by the dyer and calico-printer in the production of black and brown colours. When a solution of sulphate of manganese is mixed with solution of chloride of lime (p. 145), it gives a black precipitate of hydrated peroxide of manganese—

$$2(MnO.SO_3) + CaO.ClO + 2CaO = 2MnO_2 + 2(CaO.SO_3) + CaCl$$

By decomposing a solution of sulphate of manganese with potash or soda, a white precipitate of *hydrated protoxide of manganese* is obtained, which becomes brown when exposed to the air, absorbing oxygen, and becoming converted into the hydrated sesquioxide of manganese.

If solution of sulphate of manganese be mixed with carbonate of soda, a white precipitate of *carbonate of manganese*, $2(MnO.CO_2).HO$, is obtained. The pink crystallised mineral *manganese spar* consists of carbonate of manganese ($MnO.CO_2$).

Protoxide of manganese (MnO) itself is obtained as a green powder by heating carbonate of manganese in a tube through which hydrogen is passed to exclude the air, which would convert the protoxide into red oxide (Mn_3O_4). The protoxide has been obtained in transparent emerald-green crystals.

Sesquioxide of manganese, crystallised in octahedra, forms the mineral *braunite*, and, in combination with water, the prismatic crystals of *manganite* ($Mn_2O_3.HO$), which often occurs in the commercial ores of manganese. The sesquioxide is a weak base, dissolving in acids to form deep red solutions, which evolve oxygen when heated, leaving salts of the protoxide of manganese. The sulphate of sesquioxide of manganese combines with sulphate of potash to form *manganese-alum*—

$$KO.SO_3, Mn_2O_3.3SO_3 + 24Aq.$$

corresponding in crystalline form, as in composition, to alumina-alum. When binoxide of manganese in minute quantity is added to melted glass, it imparts a purple colour, which is probably due to the formation of a silicate of sesquioxide of manganese. The amethyst is believed by some to owe its colour to the same cause.

Red oxide of manganese (Mn_3O_4) is the most stable of the oxides of this metal, and is formed when either of the others is heated in air. Thus obtained, it has a brown or reddish colour; but it is found in nature as the black mineral *hausmannite*. In composition it resembles the magnetic oxide of iron, but it seems probable that its true formula is $2MnO.MnO_2$, for when treated with diluted nitric acid it leaves the black hydrated binoxide.

When a compound containing manganese, in however small a quantity, is fused on a piece of platinum foil with carbonate of soda (fig. 112), a mass of manganate of soda ($NaO.MnO_3$) is formed, which is green while hot, and becomes blue on cooling. The oxygen required to convert the lower oxides of manganese into manganic acid has been absorbed from the air.

Manganic acid is obtained in combination with potash, by mixing finely powdered binoxide of manganese into a paste with an equal weight

of hydrate of potash dissolved in a little water, drying the paste, and heating it to dull redness in a glass tube, through which oxygen is passed as long as it is absorbed. When the mass is treated with a little cold water, it gives a dark emerald-green solution, and by evaporating this over oil of vitriol, *in vacuo*, dark-green crystals of *manganate of potash* ($KO.MnO_3$) are formed, which have the same crystalline form as those of sulphate of potash. These crystals dissolve unchanged in water containing potash; but when dissolved in pure water, they yield a red solution of permanganate of potash, and a precipitate of binoxide of manganese—

$$3(KO.MnO_3) + 2HO = KO.Mn_2O_7 + MnO_2 + 2(KO.HO).$$

The change is more completely effected by adding a little free acid, even carbonic acid. The changes of colour thus produced have acquired for the manganate of potash the name *chameleon mineral*. The solution of manganate of potash (containing free potash) is very easily decomposed by substances having an attraction for oxygen. Thus, most organic substances abstract oxygen from it, and cause the separation of brown sesquioxide of manganese; filtering its solution through paper will even effect this change. The offensive emanations from putrefying organic matters are at once oxidised and rendered inodorous by manganate of potash or soda.

Manganate of soda ($NaO.MnO_3$) obtained by heating binoxide of manganese with hydrate of soda, under free exposure to air, is employed in a state of solution in water, as *Condy's green disinfectant fluid*.

The temporary formation of manganic acid affords a probable explanation of the effect of binoxide of manganese in facilitating the disengagement of oxygen from chlorate of potash (p. 14).

Permanganic acid has been obtained in a hydrated crystalline state by decomposing the permanganate of baryta with sulphuric acid, and evaporating the solution *in vacuo*. It is a brown substance, easily dissolving in water to a red liquid, which is decomposed at about 90° F., evolving oxygen, and depositing binoxide of manganese.

Permanganate of potash is largely used in many chemical operations. In order to prepare it, 4 parts of finely powdered binoxide of manganese are intimately mixed with 3½ parts of chlorate of potash, and 5 parts of hydrate of potash dissolved in a very little water. The pasty mass is dried, and heated to dull redness for some time in an iron tray or earthen crucible. The oxygen derived from the chlorate of potash converts the binoxide of manganese into manganic acid, which combines with the potash of the hydrate. On treating the cold mass with water, the manganate of potash is dissolved, forming a dark-green solution. This is diluted with water, and a stream of carbonic acid gas passed through it as long as any change of colour is observed; the carbonic acid combines with the excess of potash, the presence of which conferred stability upon the manganate, which is then decomposed into permanganate of potash and binoxide of manganese. The latter is allowed to settle, and the clear red solution poured off and evaporated to a small bulk. On cooling, it deposits prismatic crystals of the permanganate of potash ($KO.Mn_2O_7$), which are red by transmitted light, but reflect a dark-green colour. The carbonate of potash, being much more soluble in water, is left in the solution. Permanganate of potash is remarkable for its great colouring *power, a very small quantity of* the salt producing an intense purplish-

red colour in a large quantity of water. Its solution in water is ... easily decomposed by substances having an attraction for oxygen, ... sulphurous acid or a ferrous salt, the permanganic acid being red... protoxide of manganese, so that the solution becomes colourless. If ... small piece of iron wire be dissolved in diluted sulphuric acid, the ... tion of ferrous sulphate so produced will decolorise a large volu... weak solution of the permanganate, being converted into ferric sulph...

$$KO.Mn_2O_7 + 10(FeO.SO_3) + 8(HO.SO_3) = KO.SO_3 + 2(MnO.SO_3) + 5(Fe_2O_3.3SO_3) + 8HO.$$

This decomposition forms the basis of a valuable method for deter... the proportion of iron in its ores.

Many organic substances are easily oxidised by permanganate of p... and this is the case especially with the offensive emanations from puti... organic matter. Hence it is extensively used, under the name of *C... red disinfecting fluid*, in cases where a solid or liquid substance is to ... deodorised.

225. *Chlorides of manganese.*—There appear to be three compou... of manganese with chlorine, corresponding to three of the oxides, ... MnCl, Mn_2Cl_3, and $MnCl_2$; but only the first is obtainable in the ... state, the others forming solutions, which are easily decomposed ... evolution of chlorine.

The *protochloride of manganese* (MnCl) is obtained in large quantity, as a ... product in the preparation of chlorine, for the manufacture of bleaching-pow... Since there is no useful application for it, the manufacturer sometimes recon... it into the black oxide. As the native binoxide always contains iron, the li... obtained by treating it with hydrochloric acid contains sesquichloride of ... (Fe_2Cl_3) mixed with chloride of manganese (MnCl). In order to separate the ir... advantage is taken of the circumstance that sesquioxides are weaker bases than th... protoxides, so that if a small proportion of lime be added to the solution, the iron may be precipitated as sesquioxide, without decomposing the chloride of manganese—

$$Fe_2Cl_3 + 3CaO = Fe_2O_3 + 3CaCl.$$

The solution of chloride of manganese is then mixed with chalk, and subjected to the action of steam at a pressure of about two atmospheres. Carbonate of manganese is precipitated ($MnCl + CaO.CO_2 = CaCl + MnO.CO_2$), and when this is dried and heated to about 600° in a current of moist air, the carbonic acid is expelled, and a large proportion of the oxide of manganese is converted into binoxide, which may be employed again for the preparation of chlorine.

By dissolving permanganate of potash in oil of vitriol, and adding fragments of fused chloride of sodium, a remarkable greenish-yellow gas is obtained, which gives purple fumes with moist air, and is decomposed by water, yielding a red solution which contains hydrochloric and permanganic acids. It, therefore, must contain manganese and chlorine, and is sometimes regarded as the perchloride (Mn_2Cl_7) corresponding to permanganic acid; but it is more probably an oxychloride of manganese (*see* chlorochromic acid).

226. *Equivalent and atomic weights of manganese.*—The chloride of manganese has been found to contain 35·5 parts (one equivalent) by weight of chlorine, and 27·5 parts of manganese; hence the equivalent of manganese is represented by 27·5.

The specific heat of manganese and its isomorphism with iron and zinc, lead to the conclusion that its atomic weight is 55 (Mn), so that it is a diatomic metal. The *atomic formula* of protoxide of manganese is MnO (O = 16), of the binoxide MnO_2, of protochloride of manganese $MnCl_2$.

The permanganates are isomorphous with the perchlorates; the atomic

mula of perchlorate of potash is $KClO_4$, and, taking the atomic ght of manganese to be 55, the atomic formula of permanganate of sh would be $KMnO_4$, whereas if 27·5 were taken for the atomic ght of the metal, the formula of this salt would be KMn_2O_4, and its logy to the perchlorate would disappear.

COBALT.

227. Some of the compounds of cobalt are of considerable importance the arts, on account of their brilliant and permanent colours. It is erally found in combination with arsenic and sulphur, forming *tin- ite cobalt*, CoAs, and *cobalt glance*, $CoAs, CoS_2$, but its ores also gene- lly contain nickel, copper, iron, manganese, and bismuth.

The metal itself is obtained by strongly heating the oxalate of cobalt $CoO.C_2O_3$) in a covered porcelain crucible. In its properties it closely sembles iron, but is said to surpass it in tenacity.

Two *oxides of cobalt* are known—the *protoxide*, CoO, which is decidedly sic, and the *sesquioxide*, Co_2O_3, which is a very feeble base. The protoxide cobalt, like those of iron and manganese, tends to absorb oxygen from e air, and when heated in air, becomes converted into $CoO.Co_2O_3$, rresponding to the magnetic oxide of iron. The commercial oxide of balt, which is employed for painting on porcelain, is obtained by roast- ng the ore, in order to expel part of the sulphur and arsenic, dissolving in hydrochloric acid, and precipitating the sesquioxide of iron by the areful addition of lime, when the remaining arsenic is also precipi- ated as arseniate of iron. Hydrosulphuric acid is passed through the cid solution to precipitate the bismuth and copper, leaving the cobalt nd nickel in solution. The latter having been boiled to expel the excess f hydrosulphuric acid, is neutralised with lime and mixed with solution f chloride of lime ($CaO.ClO + CaCl$), which precipitates the sesqui- xide of cobalt as a black powder, leaving the oxide of nickel in solution, rom which it may be precipitated by the addition of lime.

The salts of oxide of cobalt have a fine red colour in the hydrated state, or n solution, but are generally blue when anhydrous. The silicate of cobalt ssociated with silicate of potash forms the blue colour known as *smalt*, hich is prepared by roasting the cobalt-ore, so as to convert the bulk of e cobalt into oxide, leaving, however, a considerable quantity of arsenic d sulphur still in the ore. The residue is then fused in a crucible with ound quartz and carbonate of potash, when a blue glass is formed con- ining silicate of cobalt and silicate of potash, whilst the iron, nickel, and pper, combined with arsenic and sulphur, collect at the bottom of the ucible and form a fused mass of metallic appearance known as *speiss*, hich is employed as a source of nickel. The blue glass is poured into ld water, so that it may be more easily reduced to the fine powder in hich the smalt is sold. If the cobalt-ore destined for smalt be over asted, so as to convert the iron into oxide, this will pass into the smalt a silicate, injuring its colour

Zaffre is prepared by roast cobalt-ore with two or three rts of sand.

Thénard's blue consists of d phosphate of alumina, d is prepared by mixing h phosphate of cobalt d calcining in a covered cr is obtained by preci- *ating a solution of nitrate* of potash or soda.

Rinman's green is prepared by calcining the precipitate produced by carbonate of soda in a mixture of sulphate of cobalt with sulphate of zinc. It is a compound of the oxides of cobalt and zinc.

Chloride of cobalt (CoCl), obtained by dissolving oxide of cobalt in hydrochloric acid, forms red hydrated crystals, which become blue when their water is expelled. If strong hydrochloric acid be added to a red solution of this salt, it becomes blue; if enough water be now added to render it pink, the blue colour may be produced at pleasure by boiling, the solution first passing through a neutral tint. Chloride of cobalt is employed as a *sympathetic ink*, for characters written with its pink solution are nearly invisible till they are held before the fire, when they become blue, and resume their original pink colour if exposed to the air; a little chloride of iron causes a green colour.

The *sulphide of cobalt* (CoS) is obtained as a black precipitate when an alkaline sulphide is added to a solution of a salt of cobalt. A *sesquisulphide* (Co_2S_3) is found in grey octahedra, *cobalt pyrites*. The *bisulphide* (CoS_2) has been obtained artificially.

When ammonia in excess is added to a solution of a salt of cobalt, a deep red liquid is produced, which rapidly absorbs oxygen from the air, especially if hydrochlorate of ammonia be present, giving rise to the production of some remarkable and complex bases which contain the elements of ammonia and of different oxides of cobalt.

NICKEL.

228. Nickel owes its value in the useful arts chiefly to its property of imparting a white colour to the alloys of copper and zinc, with which it forms the alloy known as *German silver*. Nickel is very nearly allied to cobalt, and generally occurs associated with that metal in its ores. One of the principal ores of nickel is the *Kupfernickel* or copper-nickel, so called by the German miners because they frequently mistook it for an ore of copper; it has a reddish metallic appearance, and the formula Ni_2As. *Grey nickel ore* or *nickel glance* is an arseniosulphide of nickel, NiAs, NiS_2. *Arsenical nickel*, NiAs, corresponds to tin-white cobalt. The metal is commonly extracted from the *speiss* separated during the preparation of smalt from cobalt-ores (p. 329); the oxide of nickel prepared by the method described above, when strongly heated in contact with charcoal, yields metallic nickel containing carbon.

The pure metal is obtained by igniting the oxalate, as in the case of cobalt, which it much resembles in properties.

The *oxides of nickel* correspond in composition to those of cobalt. The salts formed by the oxide of nickel (NiO) are usually green, and give bright green solutions. The hydrated oxide has a characteristic apple-green colour, and does not absorb oxygen from the air like the hydrated oxide of cobalt. The greater facility with which the latter is converted into sesquioxide has been applied (as above described) to effect the separation of the two metals. Oxide of nickel has been found native in octahedral crystals, which have also been obtained accidentally in a copper-smelting furnace.

Sulphate of nickel ($NiO.SO_3.HO + 6Aq.$) forms fine green prismatic crystals, the water of constitution in which may be displaced by sulphate of potash, forming the *double sulphate of nickel and potash*—

$$(NiO.SO_3, KO.SO_3 + 6Aq.)$$

h crystallises so readily that it was at one time the form in which el was separated from the other metals present in its ores.

hree *sulphides of nickel* are known—a *subsulphide*, Ni_2S; a *proto-ide*, NiS, found native as *capillary pyrites*, and obtained as a black ipitate by the action of an alkaline sulphide upon a salt of nickel; and *sulphide*, NiS_2.

CHROMIUM.

29. This metal derives its name from χρῶμα, *colour*, in allusion to the ed colours of its compounds, upon which their uses in the arts chiefly end. It is comparatively seldom met with, its principal ore being the *ome-iron ore* ($FeO . Cr_2O_3$), which is remarkable for its resistance to the ion of acids and other chemical agents. It is chiefly found in Sweden, esia, and the United States, and is imported for the manufacture of *hromate of potash* ($KO . 2CrO_3$), which is one of the chief commercial npounds of chromium. The ore is first heated to redness and thrown o water, in order that it may be easily ground to a fine powder, which ixed with carbonate of potash, chalk being added to prevent the fusion he mass, and strongly heated in a current of air on the hearth of a erberatory furnace, the mass being occasionally stirred to expose a h surface to the air. The oxide of iron is thus converted into sesqui-de, and the sesquioxide of chromium (Cr_2O_3) also absorbs oxygen from air, becoming *chromic acid* (CrO_3), which combines with the potash form chromate of potash ($KO . CrO_3$). Nitre is sometimes added to ten the oxidation. On treating the mass with water, a yellow solu-n of chromate of potash is obtained, which is drawn off from the oluble residue of sesquioxide of iron and lime, and mixed with a ht excess of nitric acid—

$$\underset{\text{Chromate of potash.}}{2(KO . CrO_3)} + HO . NO_5 = \underset{\text{Bichromate of potash.}}{KO . 2CrO_3} + KO . NO_5 + HO .$$

e solution, when evaporated, deposits beautiful red tabular crystals of hromate of potash, which dissolve in 10 parts of cold water, forming acid solution. It is from this salt that the other compounds of omium are immediately derived.

Metallic chromium has received no useful application. It has been ained in octahedral crystals by the action of sodium on sesquichloride chromium, and in a pulverulent state by the action of potassium. In latter condition it is easily acted on by acids, but the crystallised omium is insoluble even in nitro-hydrochloric acid. Like aluminum, is more easily attacked by hydrated alkalies at a high temperature, lving hydrogen and producing chromates. It is remarkably infusible.

230. Oxides of chromium.—Two oxides of chromium are known in separate state—the sesquioxide, Cr_2O_3, and chromic acid, CrO_3. Pro-ide of chromium (CrO) is known in the hydrated state, and perchromic d (Cr_2O_7) is believed to exist in solution.

Chromic acid, the most important of these, is obtained by adding to e measure of a solution of bichromate of potash, saturated at 130° F., e measure and a-half of concentrated sulphuric acid, by small portions a time, and allowing the solution to cool, when chromic acid crystallises *in fine crimson needles, which* are deliquescent, very soluble in water,

and decomposed by a moderate heat into oxygen and sesquioxide chromium. Chromic acid is a powerful oxidising agent; most orga substances, even paper, will reduce it to the green sesquioxide of chromi A mixture of bichromate of potash and sulphuric acid is employed bleaching some oils, the colouring matter being oxidised at the expens the chromic acid, and sulphate of sesquioxide of chromium produced—

$$KO.2CrO_3 + 4(HO.SO_3) = KO.SO_3 + Cr_2O_3.3SO_3 + O_3 + 4HO.$$

The bichromate itself evolves oxygen when heated to bright redness, be first fused, and afterwards decomposed—

$$2(KO.2CrO_3) = 2(KO.CrO_3) + Cr_2O_3 + O_3.$$

Neutral chromate of potash ($KO.CrO_3$) is formed by adding carbo of potash to the red solution of bichromate of potash until its red co is changed to a fine yellow, when it is evaporated and allowed crystallise. It forms yellow prismatic crystals having the same form those of sulphate of potash, and is far more soluble in water than bichromate, yielding an alkaline solution. It becomes red when hea and fuses without decomposition.

Terchromate of potash ($KO.3CrO_3$) has been obtained in red cryst by adding nitric acid to the bichromate.

Chrome-yellow is the *chromate of lead* ($PbO.CrO_3$), prepared by m ing dilute solutions of acetate of lead and chromate of potash. It largely used in painting and calico-printing, and by the chemist a source of oxygen for the analysis of organic substances, since, when hea it fuses to a brown mass, which evolves oxygen at a red heat. Chro yellow being a poisonous salt, its occasional use for colouring confection is very objectionable. Chromate of lead in prismatic crystals forms rather rare *red lead ore of Siberia*, in which chromium was first discove

Orange chrome is a *basic chromate of lead* ($2PbO.CrO_3$), and may obtained by boiling the yellow chromate with lime—

$$2(PbO.CrO_3) + CaO = 2PbO.CrO_3 + CaO.CrO_3.$$

The calico-printer dyes the stuff with yellow chromate of lead, and verts it into orange chromate by a bath of lime-water.

The colour of the *ruby* (crystallised alumina) appears to be due to presence of a small proportion of chromic acid.

Sesquioxide of chromium (Cr_2O_3) is valuable as a green colour, especi for glass and porcelain, since it is not decomposed by heat. It is prep by heating bichromate of potash with one-fourth of its weight of sta the carbon of which deprives the chromic acid of half its oxygen, lea a mixture of sesquioxide of chromium with carbonate of potash, which be removed by washing with water. If sulphur be substituted the starch, sulphate of potash will be formed, which may also removed by water. When the sesquioxide of chromium is stro heated, it exhibits a sudden glow, becomes darker in colour, and soluble in acids which previously dissolved it easily; in this res it resembles alumina and sesquioxide of iron. Like these oxides, sesquioxide of chromium is a feeble base; it is remarkable for form two classes of salts containing the same proportions of acid and differing in the colour of their solutions, and in some other Thus, there are two modifications of the *sulphate of chromium*—the green sulphate, $Cr_2O_3.3SO_3 + 5Aq.$, and *phate*, $Cr_2O_3.3SO_3 + 15Aq.$ The solution of the latter

n boiled, being converted into the former. *Chrome-alum* forms dark
le octahedra ($KO.SO_3, Cr_2O_3.3SO_3 + 24Aq.$) which contain the
st modification of the sulphate; and if its solution in water be boiled,
urple colour changes to green, and the solution refuses to crystallise.*
anhydrous sulphate of chromium forms red crystals, which are in-
ble in water and acids. A green basic *borate of sesquioxide of chromium*
ed in painting and calico-printing, under the name of *vert de Guignet*,
is prepared by strongly heating bichromate of potash with 3 parts of
stallised boracic acid, when borate of potash and borate of chromium
formed, half the oxygen of the chromic acid being expelled. The borate
potash and the excess of boracic acid are afterwards washed out by
er. By reducing an alkaline chromate with hyposulphite of soda, the
mpound $Cr_2O_3.CrO_3$ has been obtained as a brown precipitate.
Protoxide of chromium (CrO) is not known in the pure state, but is
cipitated as a brown hydrate when protochloride of chromium is de-
mposed by potash. It absorbs oxygen even more readily than protoxide
iron, becoming converted into a hydrated proto-sesquioxide of chromium
$O.Cr_2O_3$), corresponding in composition to the magnetic oxide of iron.
protoxide of chromium is a feeble base; a double sulphate of protoxide
hromium and potash ($CrO.SO_3, KO.SO_3 + 6Aq.$) is known, which
the same crystalline form as the corresponding iron salt—

$$(FeO.SO_3, KO.SO_3 + 6Aq.)$$

as a blue colour, and gives a blue solution, which becomes green when
osed to air, from the formation of sesquioxide of chromium.
Perchromic acid (Cr_2O_7?) is believed to exist in the blue solution
ained by the action of binoxide of hydrogen upon solution of chromic
, but neither the acid nor its salts have been obtained in a separate
e.

31. *Chlorides of chromium.*—The *sesquichloride of chromium* (Cr_2Cl_3), obtained by
ing dry chlorine over a mixture of sesquioxide of chromium with charcoal,
ted to redness in a glass tube, is converted into vapour, and condenses upon
cooler part of the tube in shining leaflets, having a fine violet colour. Cold
er does not affect them, but boiling water slowly dissolves them to a green solu-
resembling that obtained by dissolving sesquioxide of chromium in hydrochloric
d.
Protochloride of chromium (CrCl) results from the action of hydrogen, at a red heat,
n the sesquichloride. Strange to say, it is white, and dissolves in water to form
lue solution which absorbs oxygen from the air, becoming green. It is remark-
e that if the violet sesquichloride of chromium is suspended in water, and a
nute quantity of the protochloride added, the sesquichloride immediately dis-
es to a green solution, evolving heat.
Chlorochromic acid (CrO_2Cl) is a very remarkable brown-red liquid, obtained by
stilling 10 parts of common salt and 17 of bichromate of potash, previously fused
gether and broken into fragments, with 40 parts of oil of vitriol—

$$KO.2CrO_3 + 2NaCl + 3(HO.SO_3) = KO.SO_3 + 2(NaO.SO_3) + 3HO + 2CrO_2Cl.$$

much resembles bromine in appearance, and fumes very strongly in air, the mois-
e of which decomposes its red vapour, forming chromic and hydrochloric acids;
$_2Cl + HO = CrO_3 + HCl$. It is a very powerful oxidising and chlorinating
nt, and inflames ammonia and alcohol when brought in contact with them.
t is occasionally used to illustrate the nature of [illegible] flames; for if
rogen be passed through a bottle containing [illegible] chlorochromic acid,
gas becomes charged with its vapour, and, [illegible] with a brilliant
te flame, which deposits a beautiful green film [illegible] chromium upon

* *Exposure to cold* [illegible] again converts it [illegible] violet form.

a cold surface. The name *oxychloride of chromium*, applied to this compound, is more correct than chlorochromic acid, for it is not known to form salts.

Terfluoride of chromium (CrF_3) is another volatile compound of chromium, obtained by distilling chromate of lead with fluor spar and sulphuric acid; it is a red gas, condensible to a red liquid at a low temperature. Water decomposes it, yielding chromic and hydrofluoric acids.

Sesquisulphide of chromium (Cr_2S_3) is formed when vapour of bisulphide of carbon is passed over sesquioxide of chromium heated to redness. It forms black lustrous scales resembling graphite.

232. *Equivalent and atomic weights of chromium.*—The analysis of the chromate of silver has proved it to contain 26·3 parts by weight of chromium for 108 parts (1 eq.) of silver. The isomorphism (identity of crystalline form) existing between the chromates and the sulphates, leads to the belief that they correspond in composition, so that the chromate of silver would be represented by the formula $AgO . CrO_3$, and since Ag = 108, Cr, or the equivalent of chromium, is 26·3.

The close analogy between chromium and iron renders it necessary to double the equivalent number of chromium in order to obtain its atomic weight, so that the atom of chromium would be Cr = 52·6, the metal being diatomic; and the *atomic formula* of chromic oxide would be Cr_2O_3, of chromic acid CrO_3, of chromous chloride $CrCl_2$, and of chromic chloride Cr_2Cl_6.

The molecular formula of chlorochromic acid would be $CrCl_2O_2$, representing 155·6 parts by weight. Now, the specific gravity (or weight of 1 volume) of the vapour of chlorochromic acid is 5·52, or 80 times that of hydrogen; if 1 atom (or 1 vol.) of hydrogen be taken to weigh 1, one molecule (or 2 vols.) of chlorochromic acid should weigh 160, which is sufficiently near to the weight (155·6) represented by the above formula, allowing for unavoidable experimental errors.

233. *General review of zinc, iron, cobalt, nickel, manganese, and chromium.*—Many points of resemblance will have been noticed in the chemical history of these metals to justify their being classed in the same group. They are all capable of decomposing water at a red heat, and easily displace hydrogen from hydrochloric acid. Each of them forms a base by combining with one equivalent of oxygen, and these oxides produce salts which have the same crystalline form. All these oxides, except those of zinc and nickel, easily absorb oxygen from the air, and are converted into sesquioxides. Zinc does not form a sesquioxide, and the sesquioxide of nickel is an indifferent oxide, while that of cobalt is very feebly basic; the sesquioxide of manganese is a stronger base, and the basic properties of the sesquioxides of chromium and iron are very decided. Zinc and nickel do not exhibit any tendency to form a well-marked acid oxide, but the existence of an acid oxide of cobalt is suspected; and iron, manganese, and chromium form undoubted acids with three equivalents of oxygen. Zinc and nickel are only known to form one compound with a single equivalent of chlorine; cobalt and manganese form, in addition to their protochlorides, very unstable sesquichlorides known only in solution, but iron and chromium form very stable volatile sesquichlorides. The metals composing this group are all bi-equivalent or diatomic, and are found associated in natural minerals; this is especially the case with iron, manganese, cobalt, and nickel. They are all attracted by the magnet, with the exception of zinc, and, with the same exception, require a very high temperature for their fusion. Through zinc, the metals of this group are

nected with magnesium, which resembles it in volatility, in combusti-y, and in the crystalline form of its salts. Iron and chromium con- this group with aluminum, their sesquioxides being isomorphous with ina, and their sesquichlorides volatile like that of aluminum.

COPPER.

234. Metallic copper is met with in nature more abundantly than allic iron, though the compounds of the latter metal are of more fre-nt occurrence than those of the former. A very important vein of allic copper, of excellent quality, occurs near Lake Superior in North erica, from which 6000 tons were extracted in 1858. Metallic copper lso sometimes found in Cornwall; and *copper sand*, containing metallic per and quartz, is imported from Chile.

235. *Ores of copper.*—The most important English ore of copper is *per pyrites*, which is a double sulphide, containing copper, iron, and phur in the proportions indicated by the formula $CuFeS_2$. It may be own by its beautiful brass yellow colour and metallic lustre. Copper rites is found in Cornwall and Devonshire, and is generally associated th arsenical pyrites (FeS_2. FeAs), tinstone (SnO_2), quartz, fluor-spar, and y. A very attractive variety of copper pyrites is called *variegated per ore* or *peacock copper*, in allusion to its rainbow colours; its simplest mula is Cu_3FeS_3. This variety is found in Cornwall and Killarney.

Copper glance (Cu_2S) is another Cornish ore of copper, of a dark grey lour and feeble metallic lustre.

Grey copper ore, also abundant in Cornwall, is essentially a compound the sulphides of copper and iron with those of antimony and arsenic, t it often contains silver, lead, zinc, and sometimes mercury.

Malachite, a basic carbonate of copper, is imported from Australia urra Burra), and is also found abundantly in Siberia. Green malachite, most beautifully veined ornamental variety, has the composition O . CO_2, CuO . HO, and blue malachite is $2(CuO . CO_2) . CuO . HO$.

Red copper ore (Cu_2O) is found in West Cornwall, and the black oxide uO) is abundant in the north of Chile.

236. The seat of English copper-smelting is at Swansea, which is uated in convenient proximity to the anthracite coal employed in the rnaces. The chemical process by which copper is extracted from the includes three distinct operations:—(1), the *roasting*, to expel the senic and part of the sulphur, and to convert the sulphide of iron into ide of iron; (2), the *fusion with silica*, to remove the oxide of iron as icate, and to obtain the copper in combination with sulphur only; and), the *roasting* of this combination of copper with sulphur, in order to pel the latter and obtain metallic copper.

The details of the smelting process appear somewhat complicated, cause it is divided into several stages to allow of the introduction of e different varieties of ore to be treated. Thus, the first roasting pro-ss is unnecessary for the oxides and carbonates of copper, and the fusion ith silica is not needed for those ores which are free from iron, so that ey may be introduced at a later stage in the operations.

(1.) *Calcining or roasting the ore, to expel arsenic and part of the sulphur.* *The ores having been sorted*, and broken into small pieces, are mix

so as to contain from 8 to 10 per cent. of copper, and roasted, in
ties of about three tons, for at least twelve hours, on the spacious

Fig. 238.

(H, fig. 239) of a reverberatory furnace (fig. 238), at a temperature insu
for fusion, being occasionally stirred to expose them freely to the ac
the air, which is admitted into th
nace through an opening (O) in the
the hearth upon which the ore is s
The oxygen of the air converts a p
the sulphur into sulphurous aci
and the bulk of the arsenic into ars
acid, which passes off in the fo
vapour. A part of the sulphide o
is converted into sulphate of ir
absorbing oxygen at an early stage
process, and this sulphate is after
decomposed at a higher temper
evolving sulphurous and sulphuric acids, and leaving oxide of iro
p. 322). A portion of the sulphide of copper is also converte
oxide of copper during the roasting, so that the roasted ore consists
tially of a mixture of oxide and sulphide of copper with oxid
sulphide of iron. Since the sulphide of iron is more easily oxidise
sulphide of copper, the greater part of the latter remains unaltered
roasted ore.

Fig. 239.

During the roasting of copper ore dense white fumes escape fro
furnaces. This *copper-smoke*, as it is termed, contains arsenious, su
ous, sulphuric, and hydrofluoric acids, the latter being derived fro
fluor spar associated with the ore; if allowed to escape, these
seriously contaminate the air in the neighbourhood, and copper-s
are endeavouring to apply some method of condensing, and perhap
ing them to profitable account.

(2.) *Fusion for coarse metal, to remove the oxide of iron by di
it with silicic acid at a high temperature.*—The roasted ore i
mixed with *metal-slag* from process 4, and with ores containing silic
and oxides of copper, but no sulphur; the mixture is introduce
the *ore-furnace* (fig. 240), and fused for five hours at a higher te
ture than that employed in the previous operation. In this proce
spar is sometimes added in order to increase the fluidity of the sla

The oxide of copper acts upon the sulphide of iron still conta
the roasted ore, with formation of sulphide of copper and oxide o

since there is more sulphide of iron present than the oxide of copper decompose, the excess of sulphide of iron combines with the hide of copper to form a ble compound, which sepa- s from the slag, and col- s in the form of a *matt* or *ulus* of *coarse metal*, in a ity (C) on the hearth of the nace; it is run out into a k of water (T) in order to nulate it, so that it may be ter fitted to undergo the next eration.

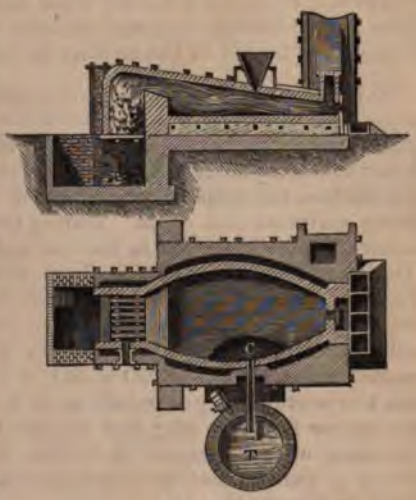


Fig. 240.

The oxide of iron combines th the silicic acid contained the charge to form a fusible icate of iron (*ore-furnace g*), which is raked out into ulds of sand, and cast into cks used for rough building rposes in the neighbourhood. The composition of the coarse tal corresponds pretty closely th the formula $CuFeS_2$. It tains from 33 to 35 per cent. of copper; whilst the original ore, before sting, is usually sorted so that it may contain about 8·5 per cent. The ore-furnace *slag* is approximately represented by the formula $O . SiO_2$; but it contains a minute proportion of copper, as is shown by e green efflorescence on the walls in which it is used around Swansea. agments of quartz are seen disseminated through this slag.

(3.) *Calcination of the coarse metal, to convert the greater part of the lphide of iron into oxide.*—The granulated coarse metal is roasted at a oderate heat for twenty-four hours, as in the first operation, so that the ygen of the air may decompose the sulphide of iron, removing the sul- ur as sulphurous acid gas, and leaving the iron in the form of oxide.

(4.) *Fusion for white metal, to remove the whole of the iron as silicate.* The roasted coarse metal is mixed with *roaster* and *refinery* slags from ocesses 5 and 6, and with ores containing carbonates and oxides of pper, and fused for six hours, as in the second operation. Any sulphide iron which was left unchanged in the roasting is now converted into ide of iron by the oxide of copper, the latter metal taking the sulphur. he whole of the oxide of iron combines with the silicic acid to form a sible slag, the composition of which is approximately represented by the rmula $3FeO . 2SiO_2$.

The *matt* or *regulus* of *white metal* which collects be[illegible] slag is arly pure subsulphide of copper (Cu_2S), half the sulp[illegible] g in the otosulphide (CuS) having been removed by oxidation[illegible]c. The hite metal is run into sand-moulds and cast into in[illegible] and her foreign metals usually collect in the lower part[illegible]t, r making *best selected copper*, the upper part is b[illegible] *parately, the inferior copper* from the b[illegible]

being termed *tile-copper*. The ingots of white metal often contain
tufts of metallic copper in the form of *copper moss*.

The slag separated from the white metal (*metal-slag*) is much
than the ore-furnace slag, and contains so much silicate of cop
is preserved for use in the melting for coarse metal.

(5.) *Roasting the white metal, to remove the sulphur and obtain
copper.*—The ingots of white metal (to the amount of about 3
placed upon the hearth of a reverberatory furnace, and heated
hours to a temperature just below fusion, so that they may be c
the surface, the sulphur passing off as sulphurous acid, and t
being converted into oxide. During this roasting the greater p
arsenic, generally present in the fine metal, is expelled as arsen
The temperature is then raised, so that the charge may be c
fused, after which it is lowered again till the 12th hour. Th
copper now acts upon the sulphide of copper to form metallic c
sulphurous acid gas, which escapes with violent ebullition
melted mass; $Cu_2S + 2CuO = SO_2 + Cu_4$. When this ebullit
the temperature is again raised so as to cause the complete se
the copper from the slag, and the metal is run out into mould
Its name of *blister copper* is derived from the appearance cau
escape of the last portions of sulphurous acid from the metal w
fying in the mould.

The slag (*roaster slag*) is formed in this operation by the co
of a part of the oxide of copper with silicic acid derived fron
adhering to the ingots, and from the hearth of the furnace.
also contains the silicates of iron and of other metals, such as tin
which might have been contained in the white metal. This sl
again in the melting for white metal.

(6.) *Refining, to remove foreign metals.*—This process consist
fusing 7 or 8 tons of the blistered copper in a reverberatory f
that the air passing through the furnace may remove any rema
phur as sulphurous acid, and may oxidise the small quantities o
lead, &c., present in the metal. Of course, a large proporti
copper is oxidised at the same time, and the suboxide of copper
with the oxides of the foreign metals, combines with silicic acid
hearth or from adhering sand) to form a slag which collects upo
face of the melted copper. A portion of the suboxide of copp
solved by the metallic copper, rendering it brittle or *dry copper*.

(7.) *Toughening or poling, to remove a part of the oxygen and
copper to tough-pitch.*—After about twenty hours, the slag is
from the metal, a quantity of anthracite is thrown over the surfa
vent further oxidation, and the metal is *poled*, *i.e.*, stirred with
young wood until a small sample, removed for examination, p
peculiar silky fracture, indicating it to be at *tough-pitch*, when
into ingots.

The chemical change during the poling appears to consist i
moval of the oxygen contained in the suboxide present in the
the reducing action of the combustible gases disengaged from
The presence of a small proportion of suboxide of copper is said
greater toughness upon the metal, so that if the poling be contin
whole of the oxygen is removed, overpoled copper of lower

1. On the other hand, the brittleness of *underpoled copper* is due resence of suboxide of copper in too large proportion. *Tough-cake* s that which has been poled to the proper extent.
n the copper is intended for rolling, a small quantity (not exceed- er cent.) of lead is generally added to it before it is ladled into the oulds.
hemical changes which take place during the above processes will e clearly understood after inspecting the subjoined table, which the composition of the products obtained at different stages of the these being distinguished by the same numerals as were employed bove description.

Products obtained in smelting Ores of Copper.

In 100 parts.	Ore.	Roasted Ore.	Coarse Metal.	Roasted Coarse Metal.	White Metal.	Blister Copper.	Refined Copper.	Tough-pitch Copper.
		(1.)	(2.)	(3.)	(4.)'	(5.)	(6.)	(7.)
. . . . .	8·2	8·6	33·7	33·7	77·4	98·0	99·4	99·6
. . . . .	17·9	17·6	33·6	33·6	0·7	0·5	trace	trace
r, ...	19·9	12·5	29·2	13·0	21·0	0·2	trace	trace
, ...	1·0	4·5	...	11·0	...	...	0·4	0·03
acid, . . .	34·3	34·3						
ric acid, . .	...	1·1						

	Ore Furnace Slag.		Metal Slag.	Roaster Slag.	Refinery Slag.	
	(2.)		(4.)	(5.)	(6.)	
of iron (FeO), ...	28·5	...	56·0	28·0	3·1	
de of copper (Cu_2O), . . .	0·5	...	0·9	16·9	36·2	
acid, ...	30·0	...	33·8	47·5	47·4	

metal is the term applied to the regulus of white metal (from process 4), still contains a considerable proportion of sulphide of iron, in consequence cient supply of oxide of copper in the furnace. *Pimple metal* is obtained in e operation when the oxide of copper is in excess, so that a portion of the s reduced, as in process 5, with evolution of sulphurous acid, which produces ply appearance in escaping. The reduced copper gives a reddish colour to ple copper. *Coarse copper* is a similar intermediate stage between white d blistered copper. *Tile copper* is that extracted from the bottoms of the f white metal, when the tops have been detached for making best select *Rosette* or *rose copper* is obtained by running water upon the toughened o as to enable the metal to be removed in films. *Anglesea* or *Mona copper* is ough copper, reduced by metallic iron from the *blue water* of the copper hich contains sulphate of copper.

For the purpose of illustration, copper may be extracted from copper pyrites mall scale in the following manner:—
rains of the powdered ore are mixed with an equal weight of dried borax, d in a covered earthen crucible (of about 8 oz. capacity), at a full red heat, t half an hour. The earthy matters associated with the ore are dissolved orax, and the pure copper pyrites collects at the bottom of the crucible. The of the latter are poured into an iron mould (such as [illegible], fig. 241). n the mass has set, it is dipped into water. The [illegible] button is ily detached from the slag by a gentle blow; it is [illegible] owdered n mortar, and introduced into an earthen crucible, [illegible] iquely ull fire, so that it may [illegible] hot enough to [illegible] should d occasionally with a [illegible] to promote the [illegible] our by *When the odour of sul[illegible]* acid is no longer [illegible] ide is

placed in a Sefström's blast-furnace (fig. 237), and exposed for a few minutes to a white heat, in order to decompose the sulphates of iron and copper. When no more fumes of sulphuric acid are perceived, the crucible is lifted from the fire, laid on the iron mortar, and the roasted ore quickly scraped out of it with a hot spatula. This mixture of the oxides of copper and iron is reduced to fine powder, mixed with 600 grains of dried carbonate of soda and 6 grains of powdered charcoal, turned to the same crucible, covered with 200 grains of dried borax

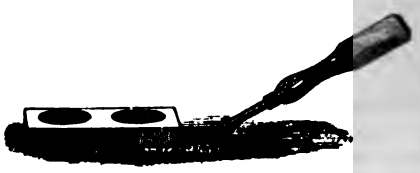


Fig. 241.

and heated in a Sefström's furnace for twenty minutes. The crucible is then allowed to cool partly, plunged into water to render it brittle, and carefully broken to extract the button of metallic copper, which is weighed to ascertain the amount contained in the original ore.

238. *Effect of impurities upon the quality of copper.*—The information possessed by chemists upon this subject is still very limited. It has been already mentioned that the presence of a small proportion of *suboxide of copper* in commercial copper is found to increase its toughness. It is believed that copper, perfectly free from metallic impurities, is not improved in quality by the presence of the suboxide, but that this substance has the effect of counteracting the red-shortness (*see* p. 315) of common copper, caused by the presence of foreign metals.

Sulphur, even in minute proportion, appears seriously to injure the malleability of copper.

Arsenic is almost invariably present in copper, very frequently amounting to 0·1 per cent., and does not appear to exercise any injurious influence in this proportion; indeed, its presence is sometimes stated to increase the malleability and tenacity of the metal.

Phosphorus is not usually found in the copper of commerce. When purposely added in quantity varying from 0·12 to 0·5 per cent. it is found to increase the hardness and tenacity of the copper, though rendering it somewhat red-short.

Tin, in minute proportion, is also said to increase the toughness of copper, though any considerable proportion renders it brittle.

Antimony is a very objectionable impurity, and is by no means uncommon in samples of copper.

Nickel is believed to injure the quality of copper in which it occurs.

Bismuth and *silver* are very generally found in marketable copper, but their effect upon its quality has not been clearly determined.

All impurities appear to affect the malleability and tenacity of copper more perceptibly at high than at low temperatures.

The conducting power of copper for electricity is affected in a extraordinary degree by the presence of impurities. Thus, if the conducting power of chemically pure copper be represented by 100, that of the pure native copper from Lake Superior has been found to be 93, that of the copper extracted from the malachite of the Burra Burra mine, South Australia was 89, whilst that of Spanish copper, remarkable as containing much arsenic, was only 14.

Pure copper is obtained by decomposing a solution of pure sulphate of copper by the galvanic current, as in the *electrotype* process. If a negative wire be attached to a copper plate immersed in the solution, pure copper may be striped off this plate in a sheet.

. *Properties of copper.* — The most prominent character which es upon copper so high a rank among the useful metals is its mal- ty, which allows it to be readily fashioned under the hammer, and to aten or rolled out into thin sheets; among the metals in ordinary nly gold and silver exceed copper in malleability, and the com- ve scarcity of those metals leads to the application of copper for purposes where great malleability is requisite.

though, in tenacity or strength, copper ranks next to iron, it is still far inferior to it, for a copper wire of $\frac{1}{10}$ inch in diameter will support 385 lbs., while a similar iron wire will carry 705 lbs. without breaking; n consequence of its inferior tenacity, copper is less ductile than iron, oes not admit of being so readily drawn into exceedingly thin wires. e comparative ease with which copper may be fused, allows it to be nuch more readily than iron; for it will be remembered that the metal can be liquefied only by the highest attainable furnace heat, as copper can be fused at about 2000° F., a temperature generally n of as a bright red heat.

being the most sonorous of metals, copper has been, from time morial, employed in the construction of bells and musical instru- s. The readiness with which it transmits electricity is turned to nt in telegraphic communication, its conducting power being almost to that of silver, which is the best of electric conductors. In con- ng power for heat, copper is surpassed only by silver and gold.

pper is not so hard as iron, and is somewhat heavier, the specific ty of cast copper being 8·92, and that of hammered or drawn copper

e resistance of copper to the chemical action of moist air gives it a advantage over iron for many uses, and the circumstance that it does decompose water in presence of acids, enables it to be employed as egative plate in galvanic couples.

0. *Effect of sea-water upon copper.*—When copper is placed in a ion of salt in water, no perceptible action takes place; but in the e of time, if air be allowed access, it becomes covered with a green ng of *oxychloride of copper* ($CuCl . 3CuO . 4HO$), the action probably sting, first, in the conversion of the copper into oxide by the air, afterwards in the decomposition of the oxide by the chloride of um; $4CuO + NaCl = CuCl . 3CuO + NaO$. The surface of the er is thus corroded, and in the case of a copper-bottomed ship, the n of sea-water not only occasions a great waste of copper, but roughens rface of the sheathing, and affords points of attachment to barnacles, which injure the speed of the vessel. Many attempts have been made viate this inconvenience. Zinc has been fastened here and there to utside of the copper, placing the latter in an electronegative con- ; the copper has been coated with various compositions, but with indifferent success. *Muntz metal*, an alloy of 3 parts of copper and rts of zinc, has been employed with some advantage in place of er, for it is very much cheaper and somewhat less easily corroded; he difficulty is by no means overcome. Copper containing about 0·5 ent. of phosphorus is said to be corroded by sea-water much less than pure copper.

1. *Danger attending the use of copper vessels in cooking food.*—The *f copper for culinary vessels* has occasionally led to serious conse-

quences, from the poisonous nature of its compounds, and from ignora of the conditions under which these compounds are formed. A perfe clean surface of metallic copper is not affected by any of the subst employed in the preparation of food, but if the metal has been allow remain exposed to the action of the air, it becomes covered with a fi oxide of copper, and this subsequently combines with water and car acid derived from the air, to produce a basic carbonate of copper,* wh becoming dissolved, or mixed with the food prepared in these v confers upon it a poisonous character. This danger may be avoid the use of vessels which are perfectly clean and bright, but even t these, certain articles of food may become contaminated with copper, this metal is much more likely to be oxidised by the air when in c tact with acids (vinegar, juices of fruits, &c.), or with fatty matter, even with common salt, and if oxide of copper be once formed, it will readily dissolved by such substances. Hence it is usual to coat the i terior of copper vessels with tin, which is able to resist the action of t air, even in the presence of acids and saline matters.

242. *Useful alloys of copper with other metals.*—The most import alloys of which copper is a predominant constituent are included in t following table :—

Composition of 100 *parts.*

	Copper.	Zinc.	Tin.	Iron.	Nickel.	Aluminum.
Brass, ...	64	36				
Muntz metal, ...	60 to 70	40 to 30				
German silver, . . .	51	30·5	...	...	18·5	
Aich (or Gedge's) metal,	60	38·2	...	1·8		
Sterro-metal, ...	55	42·4	0·8	1·8		
Bell metal, ...	78	...	22			
Speculum metal, . . .	66·6	...	33·4			
Bronze, ...	80	4	16			
Gun metal, ...	90·5	...	9·5			
Bronze coinage, . . .	95	1	4			
Aluminum bronze, . .	90	...	...	...	...	10

Brass is made by melting copper in a crucible, and adding rather more than half its weight of zinc. It is difficult to decide whether brass is a true chemical compound, or a mere mechanical mixture of copper and zinc, because it is capable of dissolving either of those metals when in a state of fusion. The circumstance that it can be deposited by decomposing a solution containing copper and zinc by the galvanic current, would appear to indicate that it is a chemical compound, and its physical properties are not such as would be expected from a mere mixture of its constituents. A small quantity of tin is added to brass intended for door-plates, which renders the engraving much easier. When it has to be turned or filed, about 2 per cent. of lead is usually added to it, in order to prevent it from adhering to the tools employed. Brass cannot be melted without losing a portion of its zinc in the form of vapour. When exposed to frequent vibration (as in the suspending chains of chandeliers) it suffers an alteration in structure and becomes extremely brittle

* Often erroneously called verdigris, which is really a basic acetate of copper.

lder used by braziers consists of equal weights of copper and zinc.
er to prevent ornamental brass-work from being tarnished by the
of air, it is either lacquered or bronzed. *Lacquering* consists
in varnishing the brass with a solution of shell-lac in spirit,
ed with dragon's blood. *Bronzing* is effected by applying a solution
nic or mercury, or platinum, to the surface of the brass. By the
of arsenious acid dissolved in hydrochloric acid, upon brass, the
acquires a coating composed of arsenic and copper, which imparts a
d appearance, the zinc being dissolved in place of the arsenic,
combines with the copper at the surface—

$$AsO_3 + 3HCl + Zn_3 = As + 3ZnCl + 3HO.$$

ture of corrosive sublimate (chloride of mercury, HgCl) and acetic
also sometimes employed, when the mercury is displaced by the
nd precipitated upon the surface of the brass, with which it forms
aze-like amalgam. For bronzing brass instruments, such as
lites, levels, &c., a solution of bichloride of platinum is employed,
ic of the brass precipitating a very durable film of metallic platinum
ts surface ($PtCl_2 + Zn_2 = Pt + 2ZnCl$). *Aich-metal* is a kind of
containing iron, and has been employed for cannon, on account
great strength. At a red heat it is very malleable.
ro-metal (στερρος, strong) is another variety of brass containing iron
n, said to have been discovered accidentally in making brass with
loy of zinc and iron obtained during the process of making gal-
d iron (p. 294). It possesses great strength and elasticity, and is
y engineers for the pumps of hydraulic presses.
minum bronze has been already noticed, and the alloys of copper
n will be described under the latter metal.
ery hard white alloy of 77 parts of zinc, 17 of tin, and 6 of copper,
metimes employed for the bearings of the driving-wheels of loco-
es.

n and steel are coated with a closely adherent film of copper, by
g them in contact with metallic zinc in an alkaline solution of oxide
per, prepared by mixing sulphate of copper with tartrate of potash
da, and caustic soda. The copper is thus precipitated upon the iron
w voltaic action, the zinc being the attacked metal. By adding a
n of stannate of soda to the alkaline copper solution, a deposit of
may be obtained.

. Oxides of copper.—Two oxides of copper are well known in the
te state, viz., the suboxide Cu_2O, and the oxide CuO. Another
Cu_4O, has been obtained in a hydrated state, and there is some
ce of the existence of an acid oxide.
black oxide of copper (*cupric oxide*), CuO, is the black layer which
ed upon the surface of the metal when heated in air. It is em-
by the chemist in the ultimate analysis of organic substances by
stion (p. 73), being prepared for this purpose by acting ur
with nitric acid to convert it into nitrate of copper (p. 126)
g this to dull redness in a rough vessel made of sheet copp
es the black oxide; $CuO.NO_5 = NO_4 + O + CuO$. At
rature the oxide fuses into a very hard mass; but it can
sed by heat. Oxide of copper water easily fr
is not dissolved by water; aci dissolve it,

salts of copper, whether the use of nitric and nitric acid for cleaning the metallic surface of copper: a blackened coin, for example, immersed in strong nitric acid, and thoroughly washed, becomes as bright when freshly cleaned. Silicic acid dissolves oxide of copper at a high temperature, forming silicate of copper, which in fusion colourless glass, during a fine green colour in glass.

Red oxide or *suboxide of copper* (*cuprous oxide*), Cu_2O, is formed by mixing 5 parts of the black oxide with 4 parts of copper filings, and heating in a closed crucible. It may also be prepared by boiling a solution of sulphate of copper with a solution containing sulphite of soda and bicarbonate of soda in equal quantities, when the suboxide of copper is precipitated as a yellow powder, which should be washed, by decantation, with boiled water—

$$2(CuO.SO_3) + 2(NaO.CO_2) + NaO.SO_2 = Cu_2O + 2(NaO.SO_3) + 2CO_2.$$

The suboxide of copper is a feeble base, but its salts are not easily obtained by direct union with acids, for these generally decompose it into metallic *copper* and oxide of copper, which combines with the acid. In the moist state it is *slowly* oxidised by the air. Ammonia dissolves the suboxide, forming a solution which is perfectly colourless until it is allowed to come into contact with air, when it assumes a fine blue colour, becoming converted into an ammoniacal solution of the oxide. If the blue solution be placed in a stoppered bottle (quite filled with it) with a strip of clean copper, it will gradually become colourless, the oxide being again reduced to suboxide, a portion of the copper being dissolved. When copper filings are shaken with ammonia in a bottle of air, the same solution is obtained, the oxidation of the copper being attended with simultaneous oxidation of a portion of the ammonia, and its conversion into nitrous acid, so that white fumes of nitrite of ammonia are formed in the upper part of the bottle. If the blue solution be poured into a large quantity of water, a light blue precipitate of hydrated oxide of copper is obtained. The ammoniacal solution of oxide of copper has the unusual property of dissolving paper, cotton, tow, and other varieties of *cellulose*, this substance being reprecipitated from the solution on adding an acid.

Suboxide of copper, added to glass, imparts to it a fine red colour, which is turned to account by the glass-maker.

Quadrant-oxide of copper, Cu_4O, has been obtained in combination with water by the action of protochloride of tin and potash upon a salt of copper.

Cupric acid is believed to be formed when metallic copper is fused with nitre and caustic potash. The mass yields a blue solution in water, which is very easily decomposed, with evolution of oxygen and precipitation of oxide of copper. The existence of an unstable oxide of copper, containing more than one equivalent of oxygen, is also rendered probable by the circumstance, that oxide of copper acts like binoxide of manganese in facilitating the disengagement of oxygen from chlorate of potash by heat (page 14).

244. *Sulphate of copper.*—The beautiful prismatic crystals known as *blue vitriol, blue stone, blue copperas*, or sulphate of copper, have been already mentioned as formed in the preparation of sulphurous acid (p. 196),

ssolving copper in oil of vitriol, a process which is occasionally em-
d for the manufacture of this salt. A considerable supply of the
ate is obtained as a secondary product in the process of silver-refin-
. 207).

e sulphate of copper is also manufactured by roasting copper pyrites
uS_2) with free access of air, when it becomes partly converted into a
ure of sulphate of iron—

$$FeCuS_2 + O_8 = FeO.SO_3 + CuO.SO_3 .$$

e sulphate of iron, however, is decomposed by the heat, losing its
uric acid, and leaving simply peroxide of iron (*see* p. 322). When
oasted mass is treated with water, the oxide of iron is left undis-
d, but the sulphate of copper enters into solution, and may be ob-
d in crystals by evaporation.

ese crystals, as they are found in commerce, are usually opaque,
if they are dissolved in hot water and allowed to crystallise slowly,
become perfectly transparent, and have then the composition ex-
ed by the formula $CuO . SO_3 + 5HO$. If the crystals be heated to
emperature of boiling water, they lose four-fifths of their water, and
ble down to a greyish white powder, which has the composition
$. SO_3 + HO$, and if this be moistened with water, it becomes very
nd resumes its original blue colour. The whitish opacity of the
ary crystals of blue stone is due to the absence of a portion of the
r of crystallisation.

e fifth equivalent of water can be expelled only at a temperature of
y 400° F., and is therefore generally called water of constitution (*see*
), the formula of the crystals being then written $CuO . SO_3 . HO + 4Aq$.
crystals dissolve in four parts of cold and two parts of boiling water.
solution reddens litmus.

e sulphate of copper is largely employed by the dyer and calico-
er, and in the manufacture of pigments. It is also occasionally used
edicine, in the electrotype process, and in galvanic batteries.

a solution of sulphate of copper be mixed with an excess of solution
otash, a blue precipitate of *hydrated oxide of copper* ($CuO . HO$) is
uced. On boiling this in the liquid, it loses its water and becomes
k oxide. The paint known as *blue verditer* is hydrated oxide of
er obtained by decomposing nitrate of copper with hydrate of lime.

hen ammonia is added to solution of sulphate of copper, a basic
hate is first precipitated, which is dissolved by an excess of ammonia
dark blue fluid. On allowing this to evaporate, dark blue crystals of
onio-sulphate of copper, $CuO . SO_3, 2NH_3, HO$, are deposited. They
their ammonia when exposed to the air.

basic sulphate of copper, $CuO . SO_3, 4(CuO . HO)$, constitutes the
ral *brochantite*.

lphate of copper cannot easily be separated by crystallisation from the
ates of iron, zinc, and magnesia, because it ble salts with
, which contain, like those sulphates, 7 equ ater. An in-
e of this is seen in the *black vitriol* obtair other-liquor
e sulphate of copper at Mansfeld, and fo k crystals
orphous with green vitriol, $FeO . SO_3 . 7H$ black
ol may be written—

$$(CuMgFeMnCoNi)O . S($$

the six isomorphous metals being interchangeable without altering the general character of the salt.

Arsenite of copper or Scheele's green has been mentioned at p. 245.

The basic *phosphates of copper* compose the minerals *tagelite* and *libethenite*.

The basic *carbonates of copper* have been noticed as forming the two beautiful minerals *blue malachite*, or *chessylite*, and *green malachite*.

Mineral green ($CuO.CO_2$, $CuO.HO$) has the same composition as green malachite, and is prepared by mixing hot solutions of carbonate of soda and sulphate of copper. When boiled in the liquid, it is gradually converted into black oxide of copper.

Silicates of copper are found in the minerals *dioptase*, or *emerald copper*, and *chrysocolla*.

245. *Chlorides of copper.*—The chloride of copper (*cupric chloride*) (CuCl) is produced by the direct union of its elements, when it forms a brown mass, which fuses easily, and is decomposed into chlorine and cuprous chloride of copper, the latter being afterwards converted into vapour. When dissolved in water, it gives a solution which is green when concentrated, and becomes blue on dilution. The hydrated chloride of copper is readily prepared by dissolving the black oxide in hot hydrochloric acid, and allowing the solution to crystallise; it forms green needle-like crystals ($CuCl.2HO$). A solution of chloride of copper in alcohol burns with a splendid green flame, and the chloride imparts a similar colour to a gas flame.

Oxychloride of copper ($CuCl.3CuO.4HO$) is found at Atacama in prismatic crystals, and is called *atacamite*. The paint *Brunswick green* has the same composition, and is made by moistening copper with solution of hydrochloric acid or of sal-ammoniac, and exposing it to the air in order that it may absorb oxygen—

$$Cu_4 + HCl + 3HO + O_4 = CuCl.3CuO.4HO.$$

The Brunswick green of the shops frequently consists of a mixture of Prussian blue, chromate of lead, and sulphate of baryta.

Subchloride of copper (*cuprous chloride*), Cu_2Cl, is formed when fine copper turnings are shaken with strong hydrochloric acid in a bottle of air ($Cu_2 + HCl + O = Cu_2Cl + HO$). The subchloride dissolves in the excess of hydrochloric acid, forming a brown solution, from which water precipitates the *white* subchloride of copper, for this is one of the few chlorides insoluble in water. When exposed to light, it assumes a purplish grey tint. It may be obtained in larger quantity by dissolving 5 parts of black oxide of copper in hydrochloric acid, and boiling with 4 parts of fine copper turnings, the brown solution being afterwards precipitated by water. If the solution be moderately diluted and set aside, it deposits tetrahedral crystals of the subchloride. Ammonia (free from air) dissolves the subchloride to a colourless liquid, which becomes dark-blue by contact with air, absorbing oxygen. The ammoniacal solution of subchloride of copper is employed as a test for acetylene (p. 84), which gives a red precipitate with it. The solution may be preserved in a colourless state by keeping it in a well-stoppered bottle, quite full, with strips of clean copper. When copper, in a finely divided state, is boiled with solution of hydrochlorate of ammonia, the solution deposits

ourless crystals of the salt $Cu_2Cl.NH_3$. If the solution of this salt exposed to the air, blue crystals are deposited, having the formula $_2Cl.NH_3 + CuCl.NH_3 + HO$, and on further exposure, a compound this last salt with hydrochlorate of ammonia is deposited. The solu-n of subchloride of copper in hydrochloric acid is employed for sorbing carbonic oxide in the analysis of gaseous mixtures (p. 252). hen this solution is exposed to air it absorbs oxygen, and deposits the ychloride of copper. A strong solution of hydrochlorate of ammonia of chloride of potassium readily dissolves the cuprous chloride, even the cold, forming soluble double chlorides. The solution in chloride potassium does not absorb oxygen quite so easily as that in hydro-lorate of ammonia.

246. *Sulphides of copper.*—Copper has a very marked attraction for phur, even at the ordinary temperature. A bright surface of copper n becomes tarnished by contact with sulphur, and hydrosulphuric acid ckens the metal. Finely divided copper and sulphur combine slowly the ordinary temperature, and when heated together, they combine with nbustion. A thick copper wire burns easily in vapour of sulphur 189). Copper is even partly converted into sulphide when boiled h sulphuric acid, as in the preparation of sulphurous acid gas. This at attraction of copper for sulphur is taken advantage of in the process *kernel-roasting* for extracting the copper from pyrites containing as le as 1 per cent. of the metal. The pyrites is roasted in large heaps 186) for several weeks, when a great part of the iron is converted o peroxide, and the copper remains combined with sulphur, forming hard kernel in the centre of the lumps of ore. This kernel contains out 5 per cent. of copper, and can be smelted with economy. Children e employed to detach the kernel from the shell, which consists of roxide of iron and a little sulphate of copper, which is washed out with ter.

The *subsulphide of copper* (Cu_2S) has been mentioned among the ores copper, and among the furnace products in smelting, when it is some-mes obtained in octahedral crystals. It is not attacked by hydrochloric id, but nitric acid dissolves it readily. *Copper pyrites* is believed to ntain the copper in the form of subsulphide, its true formula being $u_2S.Fe_2S_3$; for if the copper be present as sulphide, CuS, the iron must e present as protosulphide, and the mineral would have the formula uS.FeS. Now, FeS is easily attacked by dilute sulphuric or hydro-loric acid, which is not the case with copper pyrites. Nitric acid, how-er, attacks it violently.

Sulphide of copper (CuS) occurs in nature as *indigo-copper* or *blue pper*, and may be obtained as a black precipitate by the action of drosulphuric acid upon solution of sulphate of copper. When this ecipitate is boiled with sulphur and hydrosulphate of ammonia, it is ssolved in small quantity, and the solution on cooling deposits fine rlet needles containing a higher sulphide of copper combined with drosulphate of ammonia.

A *pentasulphide of copper* (CuS_5) is obtained by decomposing sulphate copper with pentasulphide of potassium ; it forms a black precipitate, tinguished from the other sulphides of copper by its solubility in car-nate of potash.

The sulphides of copper, when exposed to air in the presence of water,

are slowly oxidised and converted into sulphate of copper, which is dissolved by the water. It appears to be in this way that the *blue water* of the copper mines is formed.

Phosphide of copper (Cu_3P), obtained as a black powder by boiling solution of sulphate of copper with phosphorus, has been already mentioned as a convenient source of phosphuretted hydrogen. Another phosphide, obtained by passing vapour of phosphorus over finely divided copper at a high temperature, is employed in Abel's composition for magneto-electric fuzes, in conjunction with subsulphide of copper and chlorate of potash.

Silicon may be made to unite with copper by strongly heating finely divided copper with silicic acid and charcoal. A bronze-like mass is obtained, containing about 5 per cent. of silicon. It is said to rival it in ductility and tenacity, and fuses at about the same temperature as bronze.

247. *Equivalent and atomic weights of copper.*—When pure black oxide of copper is heated in hydrogen, 39·5 parts by weight of the oxide give up 8 parts (one equivalent) of oxygen, to form water with the hydrogen, leaving 31·5 parts of copper. If the black oxide, then, be regarded as containing single equivalents of its elements, the equivalent of copper will be 31·5; but if the red oxide (which contains twice as much copper in proportion to the oxygen) be supposed to contain single equivalents, that of copper would be 63. The isomorphism of the black oxide of copper with the protoxide of iron (FeO) and the oxide of zinc (ZnO), which it replaces in their sulphates without alteration of crystalline form, leads to the belief that it resembles them in composition, and that the equivalent weight of copper is 31·5.

That copper is a diatomic element, *i.e.*, that its atomic weight is twice its equivalent weight (or $Cu = 63$), is shown by its specific heat, and by the constitution of its compounds. Thus, the *nitride of copper*, NCu_3, obtained by the action of ammonia gas upon heated oxide of copper, represents ammonia (NH_3), in which three atoms of copper occupy the place of three atoms of hydrogen. The *atomic formulæ* for some of the more important compounds of copper would be—red oxide Cu_2O, black oxide CuO, subsulphide Cu_2S, sulphide CuS, cuprous chloride (subchloride) $CuCl$, cupric chloride $CuCl_2$.

LEAD.

248. Lead owes its usefulness in the metallic state chiefly to its softness and fusibility. The former quality allows it to be easily rolled into thin sheets, and to be drawn into the form of tubes or pipes; it is indeed the softest of the metals in common use, and, at the same time, the least tenacious, so that it can only be drawn with difficulty into thin wire, and is then very easily broken. The ease with which it makes a dark streak upon paper shows how readily minute particles of the metal may be abraded.

In fusibility it surpasses all the other metals commonly employed in the metallic state, except tin, for it melts at 617° F., and this circumstance, taken in conjunction with its high specific gravity (11·4), particularly adapts it for the manufacture of shot and bullets. For one of its extensive uses, however, as a covering for roofs, it would be better suited

ere lighter and less fusible, for in case of fire in houses so roofed, ll of the molten lead frequently aggravates the calamity.

h the exception, perhaps, of the ores of iron, none is more abundant s country than the chief ore of lead, *galena*, a sulphide of lead . This ore might at the first glance be mistaken for the metal from its high specific gravity and metallic lustre. It is found g extensive veins in Cumberland, Derbyshire, and Cornwall, sing a limestone rock in the two first counties, and a clay slate in st. Spain also furnishes large supplies of this important ore.

ena presents a beautiful crystalline appearance, being often found ge isolated cubes, which readily cleave or split up in directions el to their faces. Blende (sulphide of zinc) and copper pyrites ide of copper and iron) are frequently found in the same vein with , and it is usually associated with quartz (silica), heavy-spar (sul- of baryta), or fluor spar (fluoride of calcium). Considerable ities of sulphide of silver are often present in galena, and in many ens the sulphides of bismuth and antimony are found.

ugh the sulphide is the most abundant natural combination of lead, y no means the only form in which this metal is found. The metal is occasionally met with, though in very small quantity, and the ate of lead ($PbO . CO_2$), *white lead ore*, forms an important ore in nited States and in Spain. The sulphate of lead ($PbO . SO_3$) is also in Australia, and is largely imported into this country to be smelted.

. The extraction of lead from galena is effected by taking advantage circumstance, that when a combination of a metal with oxygen is to a high temperature in contact with a sulphide of the same metal, ygen and sulphur unite, and the metal is liberated.

ore having been separated by mechanical treatment as far as le from the foreign matters associated with it, is mixed with a small tion of lime, and spread over the hearth of a reverberatory furnace 42), the sides of which are considerably inclined towards the centre, o form a hollow for the reception of the molten lead.

ring the first stage of the smelting process, the object is to roast the th free access of air, exposing as large a surface as possible, on

Fig. 242.—Furnace for smelting lead-ores.

account the heat is kept below that at which galena fuses; indeed, *the first two hours, no fuel* is thrown into the grate, sufficient heat

being radiated from the sides of the furnace, which have become red during the smelting of the previous charge of ore. The ore is stirred f time to time, to expose fresh surfaces to the action of the atmospheric oxy

The effect of this roasting is to convert a portion of the sulphide of (PbS) into sulphate of lead ($PbO . SO_3$), whilst another portion loses its phur, which is evolved as sulphurous acid (SO_2), and acquires oxygen in stead, becoming converted into oxide of lead (PbO). A large proportion of galena, however, remains unoxidised. When the roasting is sufficien advanced, some fuel is thrown into the grate, some rich slags from previ smeltings are thrown on to the hearth, the damper is slightly raised, the doors of the furnace are closed, so that the charge may be heated the temperature at which the oxide and sulphate of lead act upon unaltered sulphide, furnishing metallic lead, whilst the sulphur is pelled in the form of sulphurous acid.

$$\text{Thus, } PbS + 2PbO = Pb_3 + SO_2, \text{ and}$$
$$PbO . SO_3 + PbS = Pb_2 + 2SO_2.$$

During this part of the operation, the contents of the hearth are stantly raked up towards the fire-bridge, so as to facilitate the se tion of the lead, and to cause it to run down into the hollow provide its reception. It is also found that the separation of the lead from slags is much assisted by occasionally throwing open the doors to chil furnace. After about four hours, the charge is reduced to a pretty condition, the lead having accumulated at the bottom of the depr portion of the hearth with the slag above it; this slag consists chie the silicates of lime and oxide of lead, and would have contained a l proportion of the latter, if the lime had not been added as a flux a commencement of the operation. In order still further to reduc quantity of lead in the slag, a few more shovelfuls of lime are now th into the hearth, together with a little small coal, the latter servi reduce to the metallic state the oxide of lead displaced by the lime fr combination with the silicic acid.

But since silicate of lime is far less fusible than silicate of oxide of the effect of this addition of lime is to "dry up" the slags to a semi mass, and it will now be seen that if the whole of the lime had been at the commencement of the smelting, the diminished fusibility of th would have opposed an obstacle to the separation of the metallic lea

During the last hour or so, the temperature is very considerably r and at the expiration of about six hours, when the greater portion lead is thought to have separated, the slag is raked out through one doors of the furnace, and the melted metal allowed to run out thro tap-hole in front of the lowest portion of the hearth, into an iron from which it is ladled into pig-moulds.

The rich slags, together with the layer of subsulphide of lead (which forms over the surface of the metal, are worked up again v fresh charge of ore.

In the smelting of galena a very considerable quantity of lead is c off in the form of vapour; and in order to condense this, the gases the furnace are made to pass through flues, the aggregate length of is sometimes three or four miles, before being allowed to escape u chimney. When these flues are swept, many tons of lead are reco in the forms of oxide and sulphide.

In the north of England, the smelting of lead ores is now generall

an *economico-furnace* (fig. 243), or small blast-furnace, instead of erberatory furnace described ir is supplied to the furnace hree blast-pipes (A), and the d fuel being charged in at B, runs into a cavity (C) at the the furnace, whilst the slag into a reservoir (D) outside ce. The charge is sprinkled r through the rose (E) fixed the opening into the chim- prevent it from being blown he current of air.

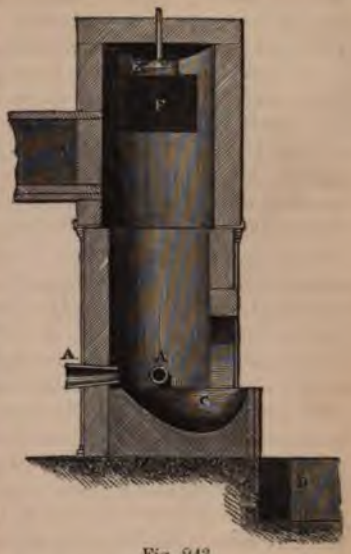


Fig. 243.

me varieties of lead, particu- smelted from Spanish ores, as *hard lead*, their hardness efly due to the presence of * and since this hardness in- naterially with some of the metal, such lead is generally to an *improving* or *calcining* which the impurities are nd removed, together with of the lead, in the dross. To six or eight tons of the hard lead are fused in an iron pot 4), and trans- a shallow cast- (C) measuring feet by five. n, which is set rth of a rever- urnace, and is it inches deep ie grate, and es at the other ead is kept in he flame which from the grate flue F, for a ying with the impurity, some being found soft after a 's calcination,

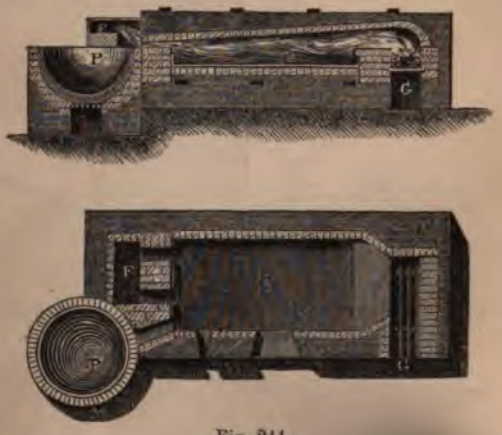


Fig. 244.

ollowing analyses illustrate the composition of hard lead :—

	English.	Spanish.
Lead,	99·27	95·81
Antimony,	0·57	3·66
Copper,	0·12	0·32
Iron,	0·04	0·21
	100	100·0

whilst others must be kept in a state of fusion for three or four
The workman judges of the progress of the operation by a peculiar
crystalline appearance assumed by a small sample on cooling.
sufficiently purified, the metal is run off and cast into pigs.

At first sight, it is not intelligible how antimony should be re
from lead by calcination, since lead is the more easily oxidised
The result must be ascribed to the tendency of antimony to form anti
acid (SbO_3) which combines with the oxide of lead. The dross (antim
of lead) formed in this process, when reduced to the metallic state,
an alloy of lead with 30 or 40 per cent. of antimony, which is much
for casting type-furniture for printers.

251. *Extraction of silver from lead.*—The lead extracted from
often contains a sufficient quantity of silver to allow of its being pro
extracted. Previously to the year 1829 this was practicable only
the lead contained more than 11 oz. of silver per ton, for the only
then known for effecting the separation of the two metals, was t
cupellation, which necessitates the conversion of the whole of the le
oxide, which has then to be separated from the silver and again r
to the metallic state, thus consuming so large an amount of labour,
considerable yield of silver must be obtained to pay for it.

By the simple and ingenious operation known as *Pattinson's desil
process*, a very large amount of the lead can be at once separated
metallic state with little expenditure of labour, thus leaving the re

Fig. 245.—Pattinson's desilverising process.

sufficiently rich in the more precious metal to defray the cost of
more expensive process of cupellation, so that 3 or 4 oz. of silver
can be extracted with profit. Pattinson founded his process u

that when lead containing a small proportion of silver is allowed to cool, being constantly stirred, a considerable quantity separates in the form of crystals containing a very minute proilver, almost the whole of this metal being left behind in the remaining liquid.

ten cast-iron pots, set in brickwork, each capable of holding s of lead, are placed in a row, with a fire-place underneath each . 245). Suppose that there are ten pots numbered consecutively, extreme left of the workman being No. 1, and that on his ht No. 10. About 6 tons of the lead containing silver are pot No. 5, the metal skimmed, and the fire raked out from that the pot may gradually cool, its liquid contents being conated with a long iron stirrer. As the crystals of lead form, ll drained in a perforated ladle (about 10 inches wide and 5) and transferred to pot No. 4. When about $\frac{4}{5}$ths of the thus been removed in the crystals, the portion still remaining h retains the silver, is ladled into pot No. 6, and the pot No. now empty, is charged with fresh argentiferous lead to be he same manner.

ts Nos. 4 and 6 have received, respectively, a sufficient quantity ls of lead and of the liquid part rich in silver, their contents ed to a perfectly similar process, the crystals of lead being ed to the left, and the rich argentiferous alloy to the right. result of these operations, the pot No. 10, to the extreme es filled with a rich alloy of lead and silver, sometimes conounces of silver to the ton, whilst pot No. 1, to the extreme s lead in which there han $\frac{1}{2}$ ounce of silver This lead is cast into market. The ladle above operation is a small *temper pot* nelted lead. A ulided at the edge of or resting the ladle haking of the crystals ff the liquid metal. present in the lead is th the silver in the n.

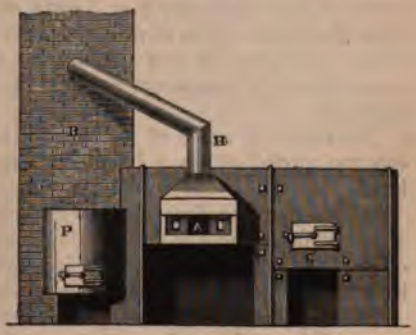


Fig. 246.—Cupellation furnace.

rder to extract the the rich alloy, it is a process of refining, *m*, which is founded idation suffered by ated in air, and upon of any tendency on silver to combine oxygen.

ry, or cupelling fur46), in which this *performed, is a reverberatory* furnace, the hearth of which con-

sists of a *cupel* (C), made by ramming moist powdered bone ashes mixed w
a little wood-ash into an oval iron frame about 4 inches deep, and provi
with four cross-bars at the bottom, each about 4 inches wide. When
frame has been well filled with bone ash, part of it is scooped out,
to leave the sides about two inches thick at the top, and three inc
the bottom, the bone-ash being left about one inch thick above the
cross-bars.

The cupel, which is about 4 feet long by 2½ feet wide, is fixed a
the flame from the grate (G) passes across it into the chimney (B),
one end, the nozzle (N) of a blowing apparatus directs a blast of air ov
surface of the contents of the cupel. The latter is carefully dried
gradually increasing heat, and is then heated to redness; the all
lead and silver, having been previously melted in an iron pot (P)
by the side of the furnace, is ladled in through a gutter until the cu
nearly filled with it; a film of oxide soon makes its appearance
the surface of the lead, and is fused by the high temperature. W
the blast is directed upon the surface, it blows off this film of oxide,
supplies the oxygen for the formation of another film upon the
metallic surface thus exposed. A part of the oxide of lead or lith
thus formed is at first absorbed by the porous material of the cupel,
the chief part of it is forced by the blast through a channel cut for
purpose in the opposite end to that at which the blast enters, and is
ceived, as it issues from A, in an iron vessel placed beneath the furn

In proportion as the lead is in this manner removed from the c
fresh portions are supplied from the adjoining melting-pot, and the p
cess is continued until about 5 tons of the alloy have been added.

The cupellation is not continued until the whole of the lead has b
removed, but until only 2 or 3 cwts. of that metal are left in combinat
with the whole of the silver (say 1000 ounces) contained in the 5 tons
alloy. The metal is run out through a hole made in the bottom of th
cupel, which is then again stopped up so that a fresh charge may be i
troduced.

The fumes of oxide of lead which are freely evolved during this pro
cess are carried off by a hood and chimney (H) situated opposite to th
blast of air.

When three or four charges have been cupelled, so as to yield from
3000 to 5000 ounces of silver, alloyed with 6 or 8 cwts. of lead, the removal
of the latter metal is completed in another cupel, since some of the silver
is carried off with the last portions of litharge.

The appearances indicating the removal of the last portion of lead are
very striking; the surface of the molten metal, which has been hitherto
tarnished, becomes iridescent as the film of oxide of lead thins off, and
afterwards resplendently bright, and when the cake of refined silver is
allowed to cool, it throws up from its surface a variety of fantastic arbores-
cent excrescences, caused by the escape of oxygen which has been mechan-
cally absorbed by the fused silver, and is given off during solidification.

The litharge obtained from the cupelling furnaces is reduced to the
metallic state by mixing it with small coal, and heating it in a furnace
similar to that employed in smelting galena.

253. On the small scale, lead may easily be extracted from galena by mixing 300
grains with 450 grains of dried carbonate of soda and 20 grains of charcoal, intro-
ducing the mixture into a crucible, and placing in it two tenpenny nails, heads down-
wards. The crucible is covered and heated in a moderate fire for about half an hour.

harcoal fire in the small furnace, fig. 117, p. 107, will suffice.) The remainder e nails is carefully removed from the liquid mass, which is then allowed to cool, crucible broken, and the lead extracted and weighed. To ascertain if it contains r, the button is placed in a small bone-ash cupel (fig. 247), heated in a muffle 248) until the whole of the lead is oxidised, and bed by the bone-ash of the cupel, leaving the te globule of silver.

Fig. 247.

all globules of lead may be conveniently cupelled harcoal before the blowpipe, by pressing some bone- nto a cavity scooped in the charcoal, placing the pon its surface, and exposing it to a good oxidising (p. 98) as long as it decreases in size. If any copper be present, the bone- will show a green stain after cooling. Pure lead gives a yellow stain. In the process the sulphur of the galena is removed, by the sodium of the carbonate, and partly e iron of the nails, the excess of carbonate of serving to flux any silica with which the a may be mixed.

Fig. 248.

4. *Uses of lead.*—The employment of metal for roofing, &c., has been already ed. Its fusibility adapts it for casting for printing, but it would be far too soft his purpose; accordingly, *type-metal* con- of an alloy of 4 parts of lead with 1 of nony. A similar alloy is used for the ts contained in shrapnel shells, since ts of soft lead would be liable to be ed together, and would not scatter so on the explosion of the shell. On the r hand, rifle-bullets are made of very pure lead, in order that they may more easily the grooves of the rifle.

mall shot are made of lead to which about bs. of arsenic per ton has been added. arsenic dissolves in the lead, hardening nd causing it to form spherical drops n chilled. The fluid metal is poured ugh a sort of colander fixed at the top of a lofty tower (or at the mouth deserted coal-shaft), and the minute drops into which it is thus divided allowed to fall into a vessel of water, after having been chilled by the n their descent. They are afterwards sorted, and polished in revolving els containing plumbago. If too little arsenic is employed, the shot elongated or pyriform; and if the due proportion has been exceeded, r form is flattened or lenticular.

ommon solder is an alloy of equal weights of lead and tin, which is e fusible than either metal separately. Other alloys containing lead be noticed in their proper places.

eaden vessels are much used in manufacturing chemistry, on account he resistance of this metal to the action of acids. Neither concen- d sulphuric, hydrochloric, nitric, or hydrofluoric acid, will act upon at the ordinary temperature. The best solvent for the metal is nitric of sp. gr. 1·2, since the nitrate of lead, being insoluble in an aci- ter strength, would be deposited upon the metal, which it woul from further action.

ead is easily corroded in situations where it is brought in cont *ighly charged with carbonic acid*, when it absorbs oxygen.

oxide of lead, which combines with [illegible] basic carbonate of lead ($PbO.CO_2$ [illegible]). [illegible] is often found converted into a white [illegible] carbonate, with a very thin film of [illegible].

When lead is exposed to the joint action of [illegible] tained in beer, wine, cider, &c., it becomes [illegible] or sugar of lead, which is very poisonous. [illegible] from the reprehensible practice of sweetening [illegible] tact with lead, and from the accidental [illegible] of shot which have been employed in clearing [illegible]. [illegible] upon leaden cisterns has been already noticed. [illegible] water soon converts lead into oxide and chloride.

255. Oxides of lead. — Four compounds of [illegible] with known—

Suboxide of lead,		[illegible]
Oxide	,,	[illegible]
Red oxide	,,	[illegible]
Peroxide	,,	[illegible]

The bright surface of lead soon tarnishes when exposed becoming coated with a dark film, which is believed to consist of lead. In a very finely divided state, lead takes fire when the air, and is converted into oxide of lead.

The *lead pyrophorus*, for exhibiting the spontaneous combustion of lead by placing some tartrate of lead in a glass tube closed at one end. Draw the tube out to a narrow neck near the [illegible], holding it nearly horizontally, while the [illegible] is heated with a gas or spirit flame as long [illegible] are evolved; the neck is then fused with a [illegible] and drawn off. The tartrate of lead [illegible] when heated, leaves a mixture of metallic [illegible] coal, which prevents it from fusing into a [illegible]. This mixture may be preserved unchanged for any length of time; but when the neck [illegible] and the contents scattered into the air, they [illegible] once, producing thick fumes of oxide of lead.

Fig. 249.

Tartrate of lead is prepared by adding ammonia to tartaric acid constantly stirred, until the bitartrate of ammonia at first formed is just [illegible] and precipitating the liquid with solution of acetate of lead. The precipitate of lead is collected upon a filter, washed several times, and dried [illegible] heat.

Oxide or *protoxide of lead* is prepared on a large scale by [illegible] in air. When the metal is only moderately heated, the [illegible] yellow powder, which is known in commerce as *massicot*, [illegible] temperature the oxide melts, and on cooling forms a brown [illegible] which is called *litharge* (λίθος, *stone*; ἄργυρος, *silver*), [illegible] that obtained by the alchemists would always furnish a [illegible] portion of silver, which was present in most samples of [illegible] introduction of Pattinson's process. The litharge of commerce [illegible] a red colour, caused by the presence of some red oxide [illegible] heated to dull redness, litharge assumes a dark brown colour [illegible] yellow on cooling. At a bright red heat it fuses, and readily [illegible] crucibles, forming a fusible silicate of lead, and soon [illegible]

a boiled with distilled water, litharge is dissolved in small quantity, ng a solution which is decidedly alkaline, and becomes turbid when ed to the air, absorbing carbonic acid, and depositing carbonate of The presence of a small quantity of saline matter in the water rs the solution of the oxide, but organic matter, and especially sugar, rs it. Two definite white *hydrates of oxide of lead*, HO . 2PbO and 3PbO, may be obtained by precipitating solutions of lead with the es. Oxide of lead is a powerful base, and has a strong tendency to basic salts. Hot solutions of potash and soda dissolve it readily, leposit it in pink crystals on cooling.

harge, from its easy combination with silicic acid at a high tempera- is much used in the manufacture of glass, and in glazing earthenware. assayer also employs it as a flux. A mixture of litharge with lime metimes applied to the hair, which it dyes of a purplish-black colour, o the formation of sulphide of lead from the sulphur existing in hair. *mastic*, used by builders in repairing stone, is a mixture of 1 part of icot with 10 parts of brickdust, and enough linseed oil to form a ; it sets into a very hard mass, which is probably due partly to the ation of silicate of lead, and partly to the *drying* of the linseed oil by ation favoured by the oxide of lead.

d lead or *minium* is prepared by heating massicot in air to about F., when it absorbs oxygen, and becomes converted into red lead. massicot for this purpose is prepared by heating lead in a reverberatory ce to a temperature insufficient to fuse the oxide which is formed, ejecting the first portions, which contain iron and other metals more oxidisable than lead (as cobalt), as well as the last, which contain r and silver, less easily oxidised than lead. The intermediate pro- is ground to a fine powder and suspended in water; the coarser les are thus separated from the finer, which are dried, and heated n trays placed in a reverberatory furnace till the requisite colour een obtained. Minium is largely used in the manufacture of whence it is necessary that it should be free from the oxides n, copper, cobalt, &c., which would colour the glass. It is also em- d as a common red mineral colour, and in the manufacture of lucifer- es.

hen minium is treated with dilute nitric acid, nitrate of lead . NO_5) is obtained in solution, and peroxide of lead (PbO_2) is left rown powder, showing that minium is probably a compound of the and peroxide of lead. The minium obtained by heating massicot till no further increase of weight is observed, has the composition). PbO_2 or Pb_3O_4, which would appear to represent pure minium; nercial minium, however, has more frequently a composition corre- ding to $3PbO . PbO_2$, but when this is treated with potash, PbO is lved out, and $2PbO . PbO_2$ remains. Minium evolves oxygen at a eat, becoming [illegible] hence the necessity for keeping the temperature 0° F. [illegible]

ide, or [illegible] *lead*, is found in the mineral as *he* [illegible] ustrous, six-sided prisms. It be prepar[illegible] in fine powder, with nitric diluted w[illegible] hing and drying. The bin- of lead ea[illegible] ubstances; sulphur, mixed it, may be [illegible] oxide is a common ingre- *in lucifer-s.* [illegible] ng property is frequently

turned to account in the laboratory, for example, in absorbing sulph... acid from gaseous mixtures by converting it into sulphate of l... $PbO_2 + SO_2 = PbO.SO_2$. Binoxide of lead is not dissolved by d... acids and has no basic properties; indeed, it is sometimes called pl... acid, for it combines with potash and soda when fused with their hyd... Plumbate of potash ($KO.PbO_2.3HO$) has been crystallised fro... alkaline solution, but is decomposed by pure water.

256. *White lead* or *ceruse* is a carbonate of oxide of lead, or, st... speaking, a basic carbonate, a combination of carbonate of oxi... lead ($PbO.CO_2$) with variable proportions of hydrated oxide of l... ($PbO.HO$). This substance is a constant product of the corrosive a... of air and water upon the metal. Its formation is, of course, very m... encouraged by the presence of organic matters in a state of decay, wh... evolve carbonic acid.

White lead is manufactured on the large scale by two processes, whi... depend, however, upon the same principle; this may be stated as follows:— when oxide of lead is brought in contact with acetic acid ($HO.C_4H_3O_3$) it displaces the water from the latter to form the acetate of lead (sugar of lead, $PbO.C_4H_3O_3$). This salt is capable of combining with twice as much oxide of lead as it at present contains, forming the tribasic acetate of lead ($3PbO.C_4H_3O_3$), and if this be acted upon by carbonic acid, two-thirds of the oxide of lead are converted into carbonate, whilst the neutral acetate of lead ($PbO.C_4H_3O_3$) is left.

In the older of the two processes, commonly known as the Dutch process, metallic lead, in the form of square gratings cast from the purest lead, is placed over earthen pots containing a small quantity of common vinegar; a number of these pots being built up into heaps, together with alternate layers of dung or spent tan, the heaps are entirely covered up with the same material. The metal is thus exposed to conditions most favourable to its oxidation, viz., a very warm and moist atmosphere produced by the fermentation of the organic matters composing the heap, and the presence of a large quantity of acid vapour generated from the acetic acid of the vinegar. The lead is therefore soon converted into oxide, a portion of which unites with the acetic acid to form the tribasic acetate of lead, which is then decomposed by the carbonic acid evolved from the fermenting dung or tan, yielding carbonate of lead, which combines with another portion of the oxide of lead and of water to form the white lead. The neutral acetate of lead left after the removal of the oxide of lead from the tribasic acetate, is now ready to take up an additional quantity of the oxide, and the process is thus continued until, in the course of a few weeks, the lead has become coated with a very thick crust of white lead; the heaps are then destroyed, the crust detached, washed, to remove adhering acetate of lead, ground to a paste with water, and dried. Rolled lead is not so easily converted as cast lead.

The newer process is a more direct application of the same principle, for it consists in boiling acetic acid with an excess of litharge in order to produce the tribasic acetate of lead, which is afterwards decomposed by passing through it a current of carbonic acid obtained by combustion or fermentation, or even by exhalation from the earth. The solution of neutral acetate of lead is then again boiled with litharge, when tribasic acetate is produced, and is again precipitated by the carbonic acid. The precipitated carbonate of lead always carries down with it a variable pro-

tion of the hydrated oxide of lead. This process is, of course, much re rapid than the old one, and dispenses with the grinding which is so rious to the workmen; but the white lead so produced, being crystal-e, has less opacity or covering-power (*body*) than that obtained by the tch method.

The usual composition of white lead is expressed by the formula O . HO, 2(PbO . CO_2), though other basic carbonates of lead are often ced with it.

White lead being very poisonous, its use by painters and others is gene-ly attended with symptoms of lead-poisoning, arising in many cases obably, from neglecting to wash the hands before eating, the effect of d being *cumulative*, so that minute doses may show their combined tion after many days. Diluted sulphuric acid and solutions of the sul-ates of magnesia and the alkalies are sometimes taken internally to unteract its effect, since the sulphate of lead is not poisonous.

All paints containing lead, and cards glazed with white lead, are ackened even by minute quantities of sulphuretted hydrogen, from the oduction of black sulphide of lead. If the blackened surface remain posed to the light and air, it is bleached again, the sulphide of lead bS) being oxidised and converted into white sulphate of lead bO . SO_3), but this does not take place in the dark. A little sulphide lead or powdered charcoal is sometimes mixed with commercial white d to give it a bluish tint.

The pure *carbonate of lead* is found in white crystals associated with lena.

Sulphate of lead is found in nature in prismatic and octahedral crystals *anglesite* or *lead-vitriol*. It is nearly insoluble in diluted acids, d is one of the chief forms in which lead is precipitated from its lutions in analytical operations. The minerals *lanarkite* and *leadhillite* e compounds of sulphate and carbonate of lead. The chromates of d have been already noticed.

Phosphate of lead ($3PbO . PO_5$) is occasionally associated with the car-nate in the ores of lead.

257. *Chloride of lead* (PbCl) forms the mineral termed *horn-lead*. It one of the few chlorides which are not readily soluble in water, and is cipitated when hydrochloric acid or a soluble chloride is added to a ution of lead. Boiling water dissolves about $\frac{1}{30}$ of its weight of chloride lead, and deposits it in beautiful shining white needles on cooling. It es easily, and is converted into vapour at a high temperature.

The *oxychloride of lead* (PbCl . PbO) is formed when chloride of lead eated in air. It is sometimes employed as a substitute for white lead painting, being prepared for this purpose by decomposing finely wdered galena with concentrated hydrochloric acid (PbS + HCl = Cl + HS) washing the resulting chloride of lead with cold water, dis-ving it in hot water, and adding lime-water, which precipitates the chloride—

$$2PbCl + CaO = PbCl . PbO + CaCl.$$

Turner's yellow (Paris yellow, patent yellow, mineral yellow) is another chloride of lead (PbCl . 7PbO), prepared by heating a mixture of harge and sal-ammoniac. It has a fine golden yellow colour, is easily ed, *and crystallises in octahedra* on cooling. The mineral *mendipite*

is an oxychloride of lead ($PbCl.2PbO$) which occurs in colourless prismatic crystals.

Iodide of lead (PbI) is obtained as a bright yellow precipitate on mixing solutions of nitrate or acetate of lead and iodide of potassium. If it be allowed to settle, the liquid poured off, and the precipitate dissolved in boiling water (with one or two drops of hydrochloric acid), it forms a colourless solution, depositing golden scales as it cools.

258. *Sulphides of lead.*—The subsulphide (Pb_2S) has been mentioned as produced in smelting galena. Sulphide of lead, or galena, has been described among the ores of lead. It is always obtained as a black precipitate when hydrosulphuric acid or a soluble sulphide acts upon a solution containing lead, even in minute proportion.

A persulphide of lead, the composition of which has not been ascertained, is formed as a red precipitate when a solution of lead is mixed with a solution of an alkaline sulphide saturated with sulphur (or with solution of hydrosulphate of ammonia which has been kept till it has acquired a red colour).

Chlorosulphide of lead ($3PbS.2PbCl$) is obtained as a bright red precipitate when hydrosulphuric acid is added in small quantity to a solution of chloride of lead in hydrochloric acid.

Selenide of lead (PbSe) occurs associated with the sulphide in some lead ores; it much resembles galena, and has the same crystalline form.

259. *Equivalent and atomic weights of lead.*—The analysis of the oxide and chloride of lead has shown that 8 parts by weight (1 eq.) of oxygen and 35·5 parts (1 eq.) of chlorine, are respectively combined with 103·5 parts of lead; the equivalent of lead, therefore, is 103·5. The specific heat of lead, and its isomorphism with other diatomic metals, show its atomic weight to be twice its equivalent weight, or 207. The *atomic formulæ* of some of its chief compounds would be—litharge $\dot{P}b\dot{O}$, minium $2\dot{P}b\dot{O}.\dot{P}b\dot{O}_2$, peroxide of lead $\dot{P}b\dot{O}_2$, galena $\dot{P}b\dot{S}$, chloride of lead $\dot{P}b\dot{C}l_2$.

260. THALLIUM.—The discovery of this metal in 1861 was one of the first results of the application of the new method of testing by observation of coloured lines in the spectrum of a flame, described at p. 273. Crookes was examining the spectrum obtained by holding in the flame of a Bunsen burner the deposit formed in the flues of a sulphuric acid chamber, in which pyrites was employed as the source of sulphur. A green line made its appearance in the spectrum, which a less acute and practised observer might have mistaken for one of the lines caused by barium (*see* fig. 221), with which it nearly coincides in position; but the line was much brighter than that produced by barium, and on instituting a searching analysis of the deposit, a metal was obtained which did not agree in properties with any hitherto described, and was named *thallium*, from θαλλός, *a young shoot*, in allusion to the vernal green colour of its spectrum line. It has since been detected in several mineral waters; but the pyrites obtained from Spain and Belgium appear to be its best source. From the flue-dust of the sulphuric acid chambers, the metal is extracted by a simple process, but large quantities must be operated on to obtain any considerable amount. The deposit is treated with boiling water, and the solution mixed with much strong hydrochloric acid, which precipitates the thallium as chloride; this is converted into acid sulphate of thallium by treatment with sulphuric acid, and this salt having been purified by recrystallisation, is decomposed by zinc, which precipitates metallic thallium in a spongy form, fusible into a compact mass in an atmosphere of coal-gas.

In external characters thallium is very similar to lead; but it tarnishes much more rapidly when exposed to air, and the streak which it makes on paper soon becomes yellowish, being converted into oxide of thallium. If a tarnished piece of the metal be allowed to touch the tongue, a strongly alkaline taste is perceived, for the oxide of thallium or *thallous oxide* (Tl_2O) is very soluble in water, so that the tarnished

l becomes bright when immersed in water. The ready solubility of the oxide ed to require thallium to be classed among the alkali-metals, a view which was naraged by the circumstance that its specific heat proved it to be monatomic like ssium and sodium. But thallium appears to be more nearly related to another atomic metal, silver, by the sparing solubility of its chloride and the insolubility s sulphide. The circumstance that it may be kept unaltered in water, and may recipitated from its salts by zinc, at once removes it from the group of alkali-als. The ready solubility of its oxide in water is only an exaggeration of the aviour of the oxides of lead and silver, both of which dissolve slightly in water, ding alkaline solutions. Diluted sulphuric acid acts upon thallium as upon evolving hydrogen. Thallium burns in oxygen with a beautiful green flame, the chlorate of thallium has been recommended for the manufacture of green s in place of chlorate of baryta (*see* p. 158). The sulphate of thallium, unlike te of lead, is easily soluble in water; the carbonate is rather sparingly soluble, far more soluble than carbonate of lead.

Thallic oxide, TlO_3, is obtained by adding hypochlorite of soda to thallous chloride ed with excess of carbonate of soda. It is also a basic oxide, its sulphate having composition $TlO_3 . 3SO_3 . HO + 6Aq$.

Salts of thallium, like those of lead, are poisonous.

The equivalent and atomic weights of thallium appear to be identical, and are ex-ssed by the number 204.

SILVER.

261. In silver, we meet with the first metal hitherto considered which not capable of undergoing oxidation in the air, under any circumstances, d this, in conjunction with its beautiful appearance, occasions its mani-ld ornamental uses, which are much favoured also by the great mal-ability and ductility of this metal (in which it ranks only second to old), for the former property enables it to be rolled out into thin plates leaves, so that a small quantity of silver suffices to cover a large surface, hilst its ductility permits the wire-drawer to produce that extremely thin lver wire which is employed in the manufacture of silver lace.

Silver, although pretty widely diffused, is found in comparatively small uantity, and hence it bears a high value, which adapts it for a medium f currency.

As might be expected from its want of direct attraction for oxygen, lver is found frequently in the metallic or native state, crystallised in ubes or octahedra, which are sometimes aggregated together, as in the lver-mines of Potosi, into arborescent or *dendritic* forms. Silver is more equently met with, however, in combination with sulphur, forming the lphide of silver (AgS), which is generally associated with large quantities the sulphides of lead, antimony, and iron. The largest supplies of silver e obtained from the Mexican and Peruvian mines, but the quantity rnished by Saxony and Hungary is by no means insignificant.

The process by which silver is extracted from galena has been already scribed under the history of lead.

The ores of copper (particularly the grey copper-ore) often contain so uch silver as to be worth working for that metal, in which case they e smelted in the usual way, when the copper obtained is found to con-in the whole of the silver present in the ore. This silver is separated om the copper by taking advantage of the facility with which the rmer metal is dissolved by melted lead. The process of *liquation*, as is termed, consists in fusing the argentiferous copper with about t[h] s weight of lead, and casting the alloy thus obtained into cakes or hich are afterwards gradually heated upon a hearth (fig. 250).

ved that the lead, which melts much more easily than the co[pper]

flow off in the liquid state, carrying with it, in the form of an alloy, the silver which was associated with the copper, leaving this last metal in porous masses, having the form of the original disks, upon the hearth. The lead and silver are separated by the process of cupellation (p. 353).

Fig. 250.—Liquation hearth.

When the extraction of the silver is the main object with which a particular ore is treated, the process of *amalgamation* is adopted, in which the silver is dissolved out by means of mercury. At Freiberg, the silver is extracted by this method from an ore which contains sulphide of silver together with much iron pyrites and other metallic sulphides. The ore is mixed with a small proportion of common salt, and roasted in a reverberatory furnace, when the sulphide of silver is converted into chloride of silver. It is then ground to a very fine powder, which is agitated, in revolving casks, with water and metallic iron, when the latter appropriates the chlorine and reduces the silver to the metallic state. A quantity of mercury is then introduced into the casks, and the revolution continued for several hours; the mercury dissolves the silver, copper, and lead, and is run out of the barrels into stout linen strainers, which allow the excess of fluid mercury to pass through, but retain the soft solid amalgam containing the silver. In order to recover the silver, this amalgam is placed in iron trays arranged one above the other (fig. 251), and covered with an iron bell-shaped receiver standing over water. By heaping burning fuel round the upper part of this dome, its temperature is raised sufficiently to convert the mercury into vapour, which condenses again in the water, leaving the silver, together with the copper and lead, upon the iron trays. Finally, the silver is refined by fusing it with an additional quantity of lead and subjecting the alloy to cupellation (p. 353), when the fused oxide of lead which is formed carries with it the copper, also in the form of oxide, leaving the silver in a state of purity.

Fig. 251.

Various methods have been devised to supersede the amalgamation process. For example, the ores have been roasted with common salt to convert the silver into chloride, which is dissolved out of the mass by means of a strong solution of common salt, from which the silver is afterwards precipitated in the metallic state by copper. Hyposulphite of soda has also been employed to dissolve out the chloride of silver, and the solution precipitated by sulphide of sodium, the resulting sulphide of silver being roasted to remove the sulphur and leave metallic silver.

Although silver is capable of resisting the oxidising action of the atmosphere, it is liable to considerable loss by wear and tear in consequence of its softness, and is therefore always hardened, for useful purposes, by the addition of a small proportion of copper. The standard silver employed

oinage and for most articles of silver plate, in this country, contains, 000 parts, 925 of silver and 75 of copper, whilst that used in France ains 900 of silver and 100 of copper.

andard silver, for coining and other purposes, is whitened by being ed in air and immersed in diluted sulphuric acid, which dissolves out oxide of copper, leaving a superficial film of nearly pure silver. *Dead rosted* silver is produced in this manner. *Oxidised silver* is covered a thin film of sulphide by immersion in a solution obtained by boiling hur with potash.

he solder employed in working silver consists of 5 parts of silver, 2 of , and 6 of brass.

lated articles are manufactured from copper or one of its alloys, which been united by rolling with a thin plate of silver, the adhesion of the er being promoted by first washing the surface of the copper with a tion of nitrate of silver, when a film of this metal is deposited upon surface, the copper taking the place of the silver in the solution.

Electro-plating consists in covering the surface of baser metals with a ting of silver, by connecting them with the negative (or zinc) pole of galvanic battery, and immersing them in a solution made by dissolv- cyanide of silver in cyanide of potassium ;* the current gradually de- aposes the cyanide of silver, and this metal is of course (*see* p. 21) osited upon the object connected with the negative pole, whilst the nogen liberated at the positive (copper or platinum) pole is allowed to upon a silver-plate with which this pole is connected, so that the ering solution is always maintained at the same strength, the quantity silver dissolved at this pole being precisely equal to that deposited at opposite pole.

Brass and copper are sometimes silvered by rubbing them with a mix- e of 10 parts of chloride of silver with 1 of corrosive sublimate (chlo- e of mercury) and 100 of bitartrate of potash. The silver and mercury both reduced to the metallic state by the baser metal, and an amalgam silver is formed, which readily coats the surface. The acidity of the artrate of potash promotes the reduction. The surface to be silvered uld always be cleansed from oxide by momentary immersion in nitric d, and washed with water. For *dry silvering*, an amalgam of silver and cury is applied to the clean surface, and the mercury is afterwards ex- led by heat.

Silvering upon glass is effected by means of certain organic substances ich are capable of precipitating metallic silver from its solutions. Look- glasses have been made by pouring upon the surface of plates of glass olution containing tartrate of silver and tartrate of ammonia. On heat- the glass plates to a certain temperature, the oxide of silver contained he tartrate parts with its oxygen to the tartaric acid, and the metallic er is deposited in a closely adhering film. Glass globes and vases are ered internally by a process which is exactly similar in principle.

Pure silver is easily obtained from standard silver by dissolving it in ric acid, with the aid of heat, diluting the solution with water, adding tion of common salt as long as it produces any fresh precipitate of oride of silver, washing the precipitate by decantation as long as the things give a blue tinge with ammonia, and fusing the dried precipitate

* A solution of cyanide of potassium in 10 parts of water, with 50 grains of chlor *ver dissolved in each pint of the liquid*, will answer the purpose.

with an equal weight of dried carbonate of soda in a brisk fire, wh button of silver will be found on breaking the crucible—

$$AgCl + NaO.CO_2 = Ag + NaCl + O + CO_2.$$

262. *Properties of silver.*—The brilliant whiteness of silver di guishes it from all other metals. It is lighter than lead, its sp gravity being 10·53; harder than gold, but not so hard as copper; malleable and ductile than any other metal except gold, which i passes in tenacity. It fuses at a somewhat lower temperature than g copper (about 1870° F.), and is the best conductor of heat and elect It is not oxidised by dry or moist air, either at the ordinary or at h temperatures, but is oxidised by ozone, and tarnished by air conta sulphuretted hydrogen, from the production of sulphide of silver, wh easily removed by solution of cyanide of potassium. It is unaffected dilute acids, with the exception of nitric; but hot concentrated sulp acid converts it into sulphate of silver, and when boiled with st hydrochloric acid, it dissolves to a slight extent in the form of chlorid silver, which is precipitated on adding water. The hydrates of po and soda do not act on silver to the same extent as on platinum wh fused with it; hence silver basins and crucibles are much used in t laboratory.

263. *Oxides of silver.*—There are three compounds of silver wi oxygen: the suboxide, Ag_2O; the oxide, AgO; and the peroxide, probab AgO_2, which is not known in the pure state. The oxide alone has a practical interest, as being the base contained in the salts of silver wi oxygen-acids.

Oxide of silver (AgO) is obtained as a brown precipitate when solution of nitrate of silver is decomposed by potash. It is a powerful base, slightly soluble in water, to which it imparts a weak alkaline reaction. A moderate heat decomposes it into its elements. When moist freshly precipitated oxide of silver is covered with a strong solution of ammonia, and allowed to stand for some hours, it becomes black, and acquires dangerously explosive properties. The composition of this *fulminating silver* is not accurately known, but it is supposed to be a nitride of silver, NAg_3, corresponding in composition to ammonia.

Nitrate of silver ($AgO.NO_5$), or *lunar caustic* (silver being distinguished as *luna* by the alchemists), is procured by dissolving silver in nitric acid, with the aid of a gentle heat, evaporating the solution to dryness, and heating the residue till it fuses, in order to expel the excess of acid. For use in surgery, the fused nitrate is poured into cylindrical moulds, so as to cast it into thin sticks; but for chemical purposes it is dissolved in water and crystallised, when it forms colourless square tables. The action of nitrate of silver as a caustic depends upon the facility with which it parts with oxygen, the silver being reduced to the metallic state, and the oxygen combining with the elements of the organic matter. This effect is very much promoted by exposure to sunlight or diffused daylight. Pure nitrate of silver is not changed by exposure to light, but if organic matter be present, a black deposit, containing finely divided silver, is produced. Thus, the solution of nitrate of silver stains the fingers black when exposed to light, but the stain may be removed by cyanide of potassium. If solution of nitrate of silver be dropped upon paper, and exposed to light, black stains will be produced, and the paper corroded. Nitrate of silver

frequent constituent of marking inks, since the deposit of metallic er formed on exposure to light is not removable by washing. The n is sometimes *mordanted* by applying a solution of carbonate of soda re the marking ink, when the insoluble carbonate of silver is preci- ted in the fibre, and is more easily blackened than the nitrate, espe- ly if a hot iron is applied. Marking inks without preparation are e with nitrate of silver containing an excess of ammonia, which ropriates the nitric acid, and hastens the blackening on exposure to t or heat. Hair dyes often contain nitrate of silver. The important of this salt in photography has been noticed already (p. 212).

n order to prepare nitrate of silver from standard silver (containing copper), the al is dissolved in moderately strong nitric acid, and the solution evaporated to ness in a porcelain dish, when a blue residue containing the nitrates of silver copper is obtained. The dish is now moderately heated until the residue has ed, and become uniformly black, the blue nitrate of copper being decomposed, leaving black oxide of copper, at a temperature which is insufficient to decom- e the nitrate of silver. To ascertain when all the nitrate of copper is decom- ed, a small sample is removed on the end of a glass rod, dissolved in water, ered, and tested with ammonia, which will produce a blue colour if any nitrate copper is left. The residue is treated with hot water, the solution filtered from e oxide of copper, and evaporated to crystallisation.

264. *Chloride of silver* (AgCl) is an important compound, as being e form into which silver is commonly converted in extracting it from s ores, and in separating it from other metals. It separates as a white rdy precipitate, when solution of hydrochloric acid or a chloride is ixed with a solution containing silver. The precipitate is brilliantly hite at first, but soon becomes violet, and eventually black, if exposed o daylight, or more rapidly in sunlight, the chloride of silver being educed to subchloride (Ag_2Cl), with separation of chlorine (*see* p. 212). The blackening takes place more rapidly in the presence of an excess of nitrate of silver or of organic matter, upon which the liberated chlorine is apable of acting. The chloride of silver formed by suspending silver leaf in a bottle of chlorine gas is not blackened by light. If the white hloride of silver be dried in the dark, and heated in a crucible, it fuses t about 500° F. to a brownish liquid, which solidifies, on cooling, to a transparent, nearly colourless mass, much resembling horn in external haracters (*horn silver*); a strong heat converts it into vapour, but does ot decompose it. If fused chloride of silver be covered with hydro- hloric acid, and a piece of zinc placed upon it, it will be found entirely educed, after a few hours, to a cake of metallic silver; the first portion of lver having been reduced in contact with the zinc, and the remainder by he galvanic action set up by the contact of the two metals beneath the id. Ammonia readily dissolves chloride of silver, and the solution eposits colourless crystals of the chloride when evaporated. If the mmonia be very strong, the solution deposits a crystalline compound of loride of silver with ammonia. The absorption of ammoniacal gas by loride of silver has been noticed at p. 116, and the photographic appli- tion of the chloride at p. 212.

Recovery of silver from old photographic baths.—One of the simplest methods f fecting this consists in mixing the liquid with solution of common salt as lo causes a fresh precipitate of chloride of silver, which is allowed to subside. ice or twice by decantation, mixed with a little sulphuric acid, a lum pelter) placed in it, and left for a day or two to reduce the silver to t ate. *The zinc is then taken out,* and the metallic silver well washed

tion, till the washings are quite tasteless. It may either be reconverted into nitrate by dissolving in nitric acid (p. 364), or fused in an earthen crucible with a little borax.

From the fixing solutions containing hyposulphite of soda, the silver cannot be precipitated by salt, because the chloride of silver is soluble in the hyposulphite. A piece of sheet copper left in this for a day or two will precipitate the silver at once in the metallic state.

Subchloride of silver (Ag_2Cl) has been obtained by the action of perchloride of iron upon metallic silver ($Ag_2 + Fe_2Cl_3 = Ag_2Cl + 2FeCl_2$). It is black and insoluble in nitric acid. Ammonia decomposes it, dissolving out chloride of silver, and leaving metallic silver.

Bromide of silver (AgBr) is a rare Chilian mineral. Associated with chloride of silver, it forms the mineral *embolite*. It much resembles the chloride, but is somewhat less easily dissolved by ammonia.

Iodide of silver (AgI) is also found in the mineral kingdom. It is worthy of remark that silver decomposes hydriodic acid much more easily than hydrochloric acid, forming iodide of silver, and evolving hydrogen. The iodide of silver dissolves in hot hydriodic acid, and is deposited in crystals on cooling. By adding nitrate of silver to iodide of potassium, the iodide of silver is obtained as a yellow precipitate which, unlike the chloride, does not dissolve in ammonia. Iodide of silver dissolves in a boiling saturated solution of nitrate of silver, and the solution, on cooling, deposits crystals having the composition $AgI . AgO . NO_5$, which are far more sensitive to the action of light than iodide of silver itself, a circumstance which is taken advantage of by photographers. The crystals are decomposed by water, with separation of iodide of silver.

Sulphide of silver (AgS) is found as *silver glance*, which may be regarded as the chief ore of silver; it has a metallic lustre, and is sometimes found in cubical or octahedral crystals. The minerals known as *rosiclers* or *red silver ores* contain sulphide of silver combined with the sulphides of arsenic and antimony. The black precipitate obtained by the action of hydrosulphuric acid upon a solution of silver is the sulphide of silver. It may also be formed by heating silver with sulphur in a covered crucible. Sulphide of silver is remarkable for being soft and malleable, so that medals may even be struck from it. It is not dissolved by diluted sulphuric or hydrochloric acid, but nitric acid readily dissolves it. Metallic silver dissolves sulphide of silver when fused with it, and becomes brittle even when containing only 1 per cent. of the sulphide.

265. *Equivalent and atomic weights of silver.*—When finely divided silver is heated in a current of chlorine gas, 108 parts by weight of silver combine with 35·5 parts (1 eq.) of chlorine; hence 108 is taken to represent the equivalent of silver. The specific heat of silver shows its atomic weight to be represented by the same number as its equivalent, so that it is a monatomic element, and the *atomic formulæ* of its principal compounds are written thus: Oxide of silver, Ag_2O; chloride of silver, AgCl; sulphide of silver, Ag_2S.

MERCURY.

366. Mercury (*quicksilver*) is the only metal which is liquid at the inary temperature, and since it requires a temperature of 39° below F. to solidify it, this metal is particularly adapted for the construc- of thermometers and barometers. Its high boiling point (662° F.) recommends it for the former purpose, as does its high specific gravity ·54) for the latter, a column of about 30 inches in height being able counterpoise a column of atmospheric air having the same sectional a, and a height equal to that of the atmosphere above the level of the sea. e symbol for mercury (Hg) is derived from the Latin name for this ele- nt, *hydrargyrum* (ὕδωρ, *water*, referring to its fluidity, ἄργυρον, *silver*). Mercury is not met with in this country, but is obtained from Idria ustria), Almaden (Spain), China, and New Almaden (California). It urs in these mines partly in the metallic state, diffused in minute bules or collected in cavities, but chiefly in the state of cinnabar, which a sulphide of mercury (HgS).

The metal is extracted from the sulphide at Idria by roasting the ore a kiln (fig. 252), which is connected with an extensive series of con-

Fig. 252.—Extraction of mercury at Idria.

nsing chambers built of brick-work. The sulphur is converted, by the r in the kiln, into sulphurous acid gas, whilst the mercury passes off in pour and condenses in the chambers.

At Almaden the extraction is conducted upon the same principle, but e condensation of the mercury is effected in earthen receivers (called *udels*) opening into each other, and delivering the mercury into a gutter hich conveys it to the receptacles.

The cinnabar is placed upon the arch (A, fig. 253) of brick-work, in hich there are several open- gs for the passage of the flame f the wood fire kindled at B; his flame ignites the sulphide f mercury, which burns in he air passing up from be- ow, forming sulphurous acid as and vapour of mercury $HgS + O_2 = Hg + SO_2$), hich escape through the flue F) into the aludels (C), where e chief part of the mercury *ndenses, and runs down into the gutter* (G). The sulphurous acid gas

Fig. 253.

escapes through the flue (H), and any mercury which may have e
condensation is collected in the trough (D), the gas finally passi
through the chimney (E), which provides for the requisite draught.

In the Palatinate, the cinnabar is distilled in cast-iron retort
lime, when the sulphur is left in the residue as sulphide of calciu
sulphate of lime, whilst the mercury distils over—

$$4HgS + 4CaO = 3CaS + CaO.SO_3 + Hg_4.$$

The mercury found in commerce is never perfectly pure, as may be sh
scattering a little upon a clean glass plate, when it *tails* or leaves a track u
glass, which is not the case with pure mercury. Its chief impurity is lead
may be removed by exposing it in a thin layer to the action of nitric acid
with two measures of water, which should cover its surface, and be allowe
main in contact with it for a day or two, with occasional stirring. The lea
more easily oxidised and dissolved than the mercury, though a little of t
passes into solution. The mercury is afterwards well washed with water an
first with blotting-paper, and then by a gentle heat. Mercury is easily fre
mechanical impurities by filtering it through a cone of paper, round the
which a few pin-holes have been made.

267. Although mercury in its ordinary condition is not oxidised
at the ordinary temperature, it appears to undergo a partial ox
when reduced to a fine state of division, as in those medicinal p
tions of the metal which are made by triturating it with variou
stances which have no chemical action upon it, until globules of th
are no longer visible. *Blue pill* and *grey powder*, or *hydrargyru
cretâ*, afford examples of this, and probably owe much of their me
activity to the presence of one of the oxides of mercury.

268. *Uses of mercury.*—One of the chief uses to which mer
devoted is the *silvering of looking-glasses*, which is effected by mean
amalgam of tin in the following manner: a sheet of tin-foil of the sa
as the glass to be silvered is laid perfectly level upon a table, and
over with metallic mercury, a thin layer of which is afterwards
upon it. The glass is then carefully slid on to the table, so that it
may carry before it part of the superfluous mercury with the impuritie
its surface; heavy weights are laid upon the glass so as to squeeze
excess of mercury, and in a few days the combination of tin and m
is found to have adhered firmly to the glass; this coating usually c
about 1 part of mercury and 4 parts of tin. In this and all other
which mercury is used (such as barometer-making) much suffering i
rienced by the operatives, from the poisonous action of the mercur

The readiness with which mercury unites with most other me
form *amalgams* is one of its most striking properties, and is tu
account for the extraction of silver and gold from their ores. The
tion of the latter metal for mercury is seen in the readiness with w
becomes coated with a silvery layer of mercury, whenever it is bro
contact with that metal, and if a piece of gold leaf be suspended at
distance above the surface of mercury, it will be found, after a ti
vered by the vapour of the metal which rises slowly even at the o
temperature. From the surface of rings which have been accid
whitened by mercury, it may be removed by a moderate heat, or b
dilute nitric acid, but the gold will afterwards require burnishing.

Zinc plates are *amalgamated*, as it is termed, for use in the g
battery, by rubbing the liquid metal over them under the surface o
sulphuric acid, which removes the coating of oxide from the surfac
zinc. The amalgam of zinc is not acted on by the diluted sulphuric a

the battery (*see* p. 20) until the *circuit* is completed, so that no zinc is ...ted when the battery is not in use. A combination of 5 parts of mercury ...d 2 parts of zinc is also used to promote the action of electrical machines. The addition of a little amalgam of sodium to metallic mercury gives it ... power of adhering much more readily to other metals, even to iron. ...ch an addition has been recommended in all cases where metallic sur... have to be amalgamated, and especially in the extraction of silver ...d gold from their ores by means of mercury.

Iron and platinum are the only metals in ordinary use which can be ...ployed in contact with mercury without being corroded by it. Mer...ury, however, adheres to platinum.

The following definite compounds of mercury with other metals have been ob...ined by combining them with excess of mercury, and squeezing out the fluid metal ...y hydraulic pressure, amounting to 60 tons upon the inch:—

Amalgam of lead,		Pb_2Hg	Amalgam of zinc,		Zn_2Hg
,,	silver,	$AgHg_2$	,,	copper,	$CuHg$
,,	iron,	$FeHg$	,,	platinum,	$PtHg_2$

The amalgam of silver ($AgHg_2$) has been found in nature, in dodecahedral crystals. A very beautiful crystallisation of the amalgam of silver (*Arbor Dianæ*) may be ...tained in long prisms having the composition $AgHg_3$, by dissolving 400 grains of ...trate of silver in 40 measured ounces of water, adding 160 minims of concentrated ...tric acid, and 1840 grains of mercury; in the course of a day or two crystals of ... or 3 inches in length will be deposited.

269. *Oxides of mercury.*—Two oxides of mercury are known, the sub...oxide Hg_2O, and the oxide HgO; both combine with acids to form salts.

Suboxide of mercury, *black oxide* or *mercurous oxide* (Hg_2O), is obtained by decomposing calomel with solution of potash, and washing with water ($Hg_2Cl + KO = Hg_2O + KCl$). It is very easily decomposed by exposure to light or to a gentle heat, into oxide of mercury and metallic mercury.

Red oxide of mercury, or *mercuric oxide* (HgO), is formed upon the surface of mercury, when heated for some time to its boiling point in contact with air. The oxide is black while hot, but becomes red on cooling. It is used under the name of *red precipitate* in ointments, and is prepared for this purpose by dissolving mercury in nitric acid, evaporating the solution to dryness, and gently calcining the nitrate of mercury ($HgO . NO_5$) until the nitric acid is expelled. The name *nitric oxide of mercury* refers to this process. It is thus obtained, after cooling, as a brilliant red crystalline powder, which becomes nearly black when heated, and is resolved into its elements at a red heat. It dissolves slightly in water, and the solution has a very feeble alkaline reaction. A bright yellow modification of the oxide is precipitated when a solution of corrosive sublimate is decomposed by potash ($HgCl + KO = HgO + KCl$); the yellow variety is chemically more active than the red.

When oxide of mercury is acted on by strong ammonia, it becomes converted into a yellowish white powder which possesses the properties of a strong base, absorbing carbonic acid eagerly from the air, and combining readily with other acids. It is easily decomposed by exposure to light, and, if rubbed in a mortar when dry, is decomposed with slight detonations, a property in which it feebly resembles fulminating silver (p. 364). The composition of this substance is represented by the formula $4HgO . NH_3 . 2HO$, and it is sometimes called *ammoniated oxide of mercury*. When exposed *in vacuo* over oil of vitriol, it loses $2HO$, becoming $4HgO . NH_3$, but if heated to about 260° F., it evolves another equivalent of water and becomes brown.*

* It has been stated that by heating it for some time in a current of dry ammonia, the whole of the hydrogen may be expelled as water, leaving the oxide of tetra-mercurammonium, NHg_4O, which is very explosive, and combines with water to form a hydrate which *produces salts with the acids.*

it now contains $Hg_4O_3NH_2$, and may be regarded as a compound of oxide of mercury with ammonia in which one equivalent of hydrogen is displaced by mercury ($NH_2Hg, 3HgO$), a view which would explain, in a simple manner, the evolution of ammonia when the substance is fused with hydrate of potash—

$$NH_2Hg, 3HgO + KO.HO = NH_3 + 4HgO + KO.$$

This substance is sometimes called *mercuramine;* it forms salts with the acids; *sulphate of mercuramine* has the composition $(NH_2Hg, 3HgO)SO_3$.

By passing ammonia gas over the yellow oxide of mercury as long as it is absorbed and heating the compound to about 260° F. in a current of ammonia as long as water is evolved, a brown explosive powder is obtained, which is believed to be *nitride of mercury*, NHg_3, representing ammonia in which the hydrogen has been displaced by mercury. It yields salts of ammonia when decomposed by hydrated acids.

270. The salts formed by the oxides of mercury with the oxygen-acids are of great practical importance. *Protonitrate of mercury* or *mercurous nitrate* is obtained when mercury is dissolved in nitric acid diluted with five volumes of water; it may be procured in crystals having the composition $Hg_2O.NO_5$, 2Aq. The prismatic crystals which are sometimes sold as protonitrate of mercury consist of a basic salt, $3(Hg_2O.NO_5), Hg_2O.HO$, prepared by acting with diluted nitric acid upon mercury in excess. When this salt is powdered in a mortar with a little common salt it becomes black from the separation of suboxide of mercury—

$$3(Hg_2O.NO_5), Hg_2O.HO + 3NaCl = 3Hg_2Cl + 3(NaO.NO_5) + Hg_2O + HO$$

but the neutral nitrate is not blackened ($Hg_2O.NO_5 + NaCl = Hg_2Cl + NaO.NO_5$). These nitrates cannot be dissolved in water without partial decomposition and precipitation of yellow basic nitrates.

Nitrate of mercury or *mercuric nitrate* is formed when mercury is dissolved with excess of strong nitric acid, and the solution boiled. It is better to prepare it by saturating strong nitric acid, diluted with an equal measure of water, with oxide of mercury. It may be obtained in crystals of the formula $2(HgO.NO_5), Aq$. Water decomposes it, precipitating a yellow basic nitrate, which leaves oxide of mercury when long washed with water.

Sulphate of suboxide of mercury or *mercurous sulphate* ($Hg_2O.SO_3$) is precipitated as a white crystalline powder when dilute sulphuric acid is added to a solution of protonitrate of mercury.

Sulphate of mercury or *mercuric sulphate* ($HgO.SO_3$) is obtained by heating 2 parts by weight of mercury with 3 parts of oil of vitriol, and evaporating to dryness. Mercurous sulphate is first produced, and is oxidised by the excess of sulphuric acid. It forms a white crystalline powder, which is decomposed by water into a soluble acid sulphate, and an insoluble yellow basic sulphate of mercury, $HgO.SO_3.2HgO$, known as *turbith* or *turpeth* mineral, said to have been so named from its resembling in its medicinal effects the root of the *Convolvulus turpethum*.

271. CHLORIDES OF MERCURY.—The chlorides are the most important of the compounds of mercury, the subchloride being *calomel* (Hg_2Cl) and the chloride, *corrosive sublimate* (HgCl). Vapour of mercury burns in chlorine gas, corrosive sublimate being produced.

Corrosive sublimate, chloride of mercury, bichloride or *perchloride of mercury*, or *mercuric chloride*, is manufactured by heating 2 parts by weight of mercury with 3 parts of strong sulphuric acid, and evaporating to dryness, to obtain mercuric sulphate ($Hg + 2(HO.SO_3) = HgO.SO_3 + 2HO + SO_2$), which is mixed with $1\frac{1}{2}$ part of common salt and heated in glass vessels ($HgO.SO_3 + NaCl = NaO.SO_3 + HgCl$) when sulphate of soda is left, and the corrosive sublimate is converted into vapour, condensing on the cooler part of the vessel in lustrous colourless masses, which are very heavy (sp. gr. 5·4), and have a crystalline fracture. It fuses very easily (at 509° F.) to a perfectly colourless liquid, which boils at 563° F., emitting an extremely acrid vapour which destroys the sense of smell for some time. This vapour condenses

needles, or sometimes in octahedra. Corrosive sublimate dis-
in three times its weight of boiling water, but requires 16 parts
water, so that the hot solution readily deposits long four-sided
lic crystals of the salt. It is remarkable that alcohol and ether
e corrosive sublimate much more easily than water, boiling alcohol
ing about an equal weight of the chloride, and cold ether taking
-third of its weight. By shaking the aqueous solution with ether,
eater part of the corrosive sublimate will be removed, and will
dissolved in the ether which rises to the surface. Water in which
noniac has been dissolved will take up corrosive sublimate more
than pure water, a soluble double chloride (*sal alembroth*) being
, which may be obtained in tabular crystals of the composition
$3NH_4Cl$, HO. A solution of corrosive sublimate in water con-
sal-ammoniac is a very efficacious *bug-poison.*

poisonous properties of corrosive sublimate are very marked, so
s three grains having been known to cause death in the case of a
The white of egg is commonly administered as an antidote, because
own to form an insoluble compound with corrosive sublimate, so
nder the poison inert in the stomach. The compound of albumen
orrosive sublimate is also much less liable to putrefaction than
n itself, and hence corrosive sublimate is sometimes employed for
ing anatomical preparations and for preventing the decay of wood
abining with the vegetable albumen of the sap).

ride of mercury unites with many other chlorides to form soluble
salts, and with oxide of mercury, forming several *oxychlorides of*
y, which have no useful applications.

te precipitate, employed for destroying vermin, is deposited when
on of corrosive sublimate is poured into an excess of solution of
ia; $2HgCl + 2NH_3 = NH_3.HCl + NH_2Hg.HgCl.$
White precipitate.

rue constitution of white precipitate has been the subject of much discus-
t the changes which it undergoes, under various circumstances, appear to
he conclusion that it represents the hydrochlorate of ammonia, $NH_3.HCl$,
h the hydrogen of the hydrochloric acid, and one-third of that of the
a, have been displaced by mercury. When boiled with potash, it yields
a and oxide of mercury—

$$NH_2Hg.HgCl + KO.HO = NH_3 + 2HgO + KCl.$$

boiled with water, it is only partly decomposed in a similar manner, leaving
powder having the composition $(NH_2Hg.HgCl).2HgO$, produced accord-
ie equation—

$(NH_2Hg.HgCl) + 2HO = NH_3.HCl + (NH_2Hg.HgCl).2HgO.$
White precipitate. Yellow precipitate.

ound corresponding to this yellow precipitate, but containing chloride of
in place of the oxide, is precipitated when ammonia is gradually added to
of corrosive sublimate in large excess, the result being a compound of white
te with two equivalents of undecomposed chloride of mercury,—

$$(NH_2Hg.HgCl).2HgCl.$$

te precipitate be heated to about 600° F., it evolves ammonia, and yields a
e of ammoniated subchloride of mercury, $2Hg_2Cl.NH_3$, leavi
ue powder which is insoluble in water and in diluted acids.
by boiling with potash; it may be represented as a compoun
ry with hydrochlorate of ammonia in which the whole of the
placed by mercury $(NHg_2.HgCl).HgCl$.

solution of corrosive sublimate is added to a hot solution

mixed with ammonia, a crystalline deposit is obtained on cooling the liquid is known as *fusible white precipitate*, and represents hydrochlorate of amm which one-fourth of the hydrogen has been displaced by mercury, its com being $NH_2Hg.HCl$. The same compound is formed when white precip boiled with a solution of sal-ammoniac—

$$NH_2Hg.HgCl + NH_3.HCl = 2(NH_2Hg.HCl).$$

The above compounds possess a special interest for the chemist, as the among the first to attract attention to the mobility of the hydrogen in am which has since been so well exemplified in the artificial production of bases by the action of ammonia upon the iodides of the alcohol-radicals. The of these compounds to each other is here exhibited :—

White precipitate, ...	$NH_2Hg.HgCl$
Produced with corrosive sublimate in excess,	$(NH_2Hg.HgCl).2H$
„ by boiling with water, . .	$(NH_2Hg.HgCl).2H$
„ „ sal-ammoniac, .	$NH_2Hg.HCl$
„ by heating to 600°	$(NHg_2.HgCl).HgCl$

272. *Calomel, subchloride* or *protochloride of mercury*, or *me chloride* (Hg_2Cl), unlike corrosive sublimate, is insoluble in water, it is precipitated when hydrochloric acid or a soluble chloride is a mercurous nitrate. The simplest mode of manufacturing it con intimately mixing corrosive sublimate with 1 eq. of metallic mer little water being added to prevent dust, drying the mixture thor and subliming it; $HgCl + Hg = Hg_2Cl$. But it is more con made by adding another equivalent of mercury to the materials em in the preparation of corrosive sublimate. 2 parts by weight of m are dissolved, with the aid of heat, in 3 parts of oil of vitriol, a porated to dryness; $Hg + 2(HO.SO_3) = HgO.SO_3 + SO_2 +$ The residue of mercuric sulphate is intimately mixed with 2 more mercury, and the mixture afterwards triturated with $1\frac{1}{2}$ parts of c salt, until globules are no longer visible. The mixture is then he that the calomel may pass off in vapour, which condenses as a tran fibrous cake on the cool part of the subliming vessel, leaving sulp soda behind; $HgO.SO_3 + Hg + NaCl = Hg_2Cl + NaO.SO_3$ medicinal purposes the calomel is obtained in a very fine state of by conducting the vapour into a large chamber, so as to precipita a fine powder by contact with a large volume of cold air. Steam times introduced to promote its fine division. Sublimed calomel contains some corrosive sublimate, so that it must be thoroughly with water before being employed in medicine. When perfect calomel is sublimed, a little is always decomposed during the proc metallic mercury and corrosive sublimate.

Calomel is met with either as a semitransparent fibrous mas amorphous powder, with a slightly yellow tinge. It is heavier th rosive sublimate (sp. gr. 7·18), and does not fuse before sublin may be obtained in four-sided prisms by slow sublimation. Dilut will not dissolve it, but boiling nitric acid gradually converts it i curic chloride and nitrate, which pass into solution. Alkaline s convert it into black suboxide of mercury, as is seen in *black-wa* by treating calomel with lime-water ($Hg_2Cl + CaO = Hg_2O +$ Solution of ammonia converts it into a grey compound (NH_2Hg_2. which is the analogue of white precipitate ($NH_2Hg.HgCl$), co Hg_2 in place of Hg.

Mercurous iodide (Hg_2I) is a green unstable substance, formed when iodi turated with an excess of mercury and a little alcohol. The beautif

Mercuric iodide (HgI) has been noticed at p. 173. Its vapour has the remarkably high specific gravity 15·68.

If mercuric iodide be dissolved in iodide of potassium, the solution mixed with potash, and some ammonia added, a brown precipitate is formed, which may be represented by the formula $NHg_3 . HgI . 2HO$; its formation can be explained by the equation, $4HgI + 3KO + NH_3 = NHg_3 . HgI . 2HO + 3KI + HO$.

A solution of mercuric iodide in iodide of potassium, mixed with potash, is employed as one of the most delicate tests (*Nessler's test*) for ammonia in waters; $\frac{1}{100}$ gr. of ammonia in half a pint of water is distinctly recognised by the brown yellow tinge caused by this test.

273. *Sulphides of mercury.*—When mercury is triturated with sulphur, black *subsulphide of mercury* or *mercurous sulphide* (Hg_2S) is formed; it was termed by old writers *Ethiop's mineral*, and is an unstable compound easily resolvable into metallic mercury and *mercuric sulphide* (HgS). The latter has been mentioned as the principal ore of mercury, and is important as composing *vermilion*. The native sulphide of mercury, or *cinnabar*, is found sometimes in amorphous masses, sometimes crystallised in six-sided prisms varying in colour from dark brown to bright red. It may be distinguished from most other minerals by its great weight (sp. gr. 8·2), and by its red colour when scraped with a knife. Neither hydrochloric or nitric acid, separately, will dissolve it, but a mixture of the two dissolves it as mercuric chloride, with separation of sulphur. Some specimens of cinnabar have a bright red colour, so that they only require grinding and levigating to be used as vermilion; and if the brown cinnabar in powder be heated for some time to 120° F. with a solution of sulphur in potash, it is converted into vermilion.

Of the artificial sulphide of mercury there are two varieties, the black, which is precipitated when corrosive sublimate is added to hydrosulphuric acid or a soluble sulphide, and the red (vermilion), into which the black variety is converted by sublimation, or by prolonged contact with solutions of alkaline sulphides containing excess of sulphur, though, so far as is known, the conversion is effected without chemical change, the red sulphide having the same composition as the black. In Idria and Holland, 6 parts of mercury and 1 of sulphur are well agitated together in revolving casks for several hours, and the black sulphide thus obtained is sublimed in tall earthen pots closed with iron plates, when the vermilion is deposited in the upper part of the pots, and is afterwards ground and levigated. The sublimed vermilion, however, is generally inferior to that obtained by the wet process, of which there are several modifications. One of the processes consists in triturating 300 parts of mercury with 114 parts of sulphur for two or three hours, and digesting the black product, at about 120° F., with 75 parts of hydrate of potash and 400 of water until it has acquired a fine red colour. The permanence of vermilion paint is, of course, attributable to the circumstance that it resists the action of light, of oxygen, carbonic acid, aqueous vapour, and even of the sulphuretted hydrogen and sulphurous or sulphuric acid which contaminate the air of towns, whereas the red paints containing lead are blackened by sulphuretted hydrogen, and all vegetable and animal reds are liable to be bleached by atmospheric oxygen and by sulphurous acid.

When the black precipitated mercuric sulphide is boiled with solution of corrosive sublimate, it is converted into a white *chlorosulphide of mercury*, $HgCl . 2HgS$, which is also formed when a small quantity of hydrosulphuric acid is added to corrosive sublimate.

274. *Equivalent and atomic weights of mercury.*—The analysis of

red oxide of mercury proves it to contain 1 equivalent (8 parts by weigh
oxygen combined with 100 parts of mercury; therefore, assuming it
composed of one equivalent of each element, the equivalent of me
would be 100. But if the black oxide, which contains 200 of me
combined with 8 of oxygen, be regarded as composed of single equiva
that of mercury will be 200. The greater stability of the red oxide,
ever, encourages the belief that it contains one equivalent of me
and one of oxygen, for the black oxide is easily resolved into me
mercury and the red oxide. This argument also applies to other
curic compounds, which are decidedly more stable than the mer
compounds. Thus, calomel (mercurous chloride) exhibits a disp
to separate into metallic mercury and mercuric chloride, leading
belief that the equivalent of chlorine (35·5) is combined wit
equivalent (100) of mercury in the latter, and with two equivalents
in calomel. Moreover, the strongly basic character of the red ox
mercury classes it with the oxides of silver and lead, which were al
to contain single equivalents, whilst the feebly basic characte
instability of the mercurous oxide places it on a par with the sul
of copper.

In determining the *atomic weight* of mercury, we are able to com
with hydrogen, under similar physical conditions, for the specific
of the vapour of mercury has been found to be 6·976, or 100 times
hydrogen. If 1 vol. or 1 atom of hydrogen, therefore, be taken to
1, 1 vol. or 1 atom of mercury should weigh 100.

The specific gravity, or weight of 1 vol. of calomel vapour, is 8·3
the atom of mercury = 100, calomel will contain 2 atoms of mercu
1 atom of chlorine—

Weight of 2 vols. of mercury vapour, .	13·952
„ 1 vol. of chlorine, . . .	2·470
	16·422

which represents, as nearly as can be expected, the weight of 2 v
calomel vapour. Hence, 1 molecule (or 2 vols.) of calomel vapou
tains 2 vols. of mercury vapour (or 2 atoms) and 1 vol. (1 ato
chlorine, and its *molecular formula* should be Hg_2Cl, or the same
equivalent formula.

The specific gravity of the vapour of corrosive sublimate is 9·8—

Weight of 1 vol. of mercury vapour, .	6·976
„ 1 vol. of chlorine, . . .	2·470
	9·446

so that 1 volume of corrosive sublimate vapour contains 1 vol. of me
and 1 vol. of chlorine, thus presenting a deviation from the hydrocl
acid type, in which 1 vol. of each of the elements form 2 vols. of the
pound. In order to bring corrosive sublimate under the general rule tha
molecule of a compound body occupies two volumes, its molecular for
must be written Hg_2Cl_2, representing 2 vols. Similar reasoning le
the conclusion that the bromides of mercury have the molecular for
Hg_2Br and Hg_2Br_2, and the red iodide of mercury Hg_2I_2.

The vapour of vermilion has the specific gravity 5·51. Sinc
sulphur vapour (at 1900° F.) weighs 2·23, and is combined wi

portion of 16 to 100, the weight of mercury combined with it
ion is 13·952—

2 vols. of mercury vapour weigh .	13·952
1 vol. of sulphur vapour weighs .	2·230
	16·182

ıg as nearly as possible to three times the specific gravity of the
f vermilion. Hence, 3 vols. of vermilion vapour contain 2 vols.
ns of mercury vapour, and 1 vol. or 1 atom of sulphur vapour;
in accordance with the composition of hydrosulphuric acid, the
f mercury and 1 vol. of sulphur should be condensed into 2 vols.
maly might be explained on the supposition that the high tem-
requisite to convert the vermilion into vapour suffices to suspend
action between its elements, so that the vapour of which the
gravity is taken is not really that of the compound of mercury
hur (which should occupy two vols.), but a *mixture* of the 2 vols.
ıry vapour and 1 vol. of sulphur vapour, occupying 3 vols. This
the temporary decomposition of the vapour receives some slight
from the convertibility of the black into the red sulphide by sub-

bove considerations would lead to the adoption for vermilion of
ecular formula, Hg_2S (= 2 vols.?)
pecific heat of mercury is twice as great as it should be if its
veight be = 100, and this, conjoined with some other considera-
ıs led many chemists to adopt 200 as the atomic weight of mer-
us making it a diatomic metal. It is evident that in calomel the
ts of mercury, which are combined with 35·5 parts of chlorine,
the place of 1 part of hydrogen in hydrochloric acid, so that
sum, Hg′ (or the mercury in mercurous salts), is monatomic;
n corrosive sublimate the 200 parts of mercury are combined with
s of chlorine, and occupy the place of 2 parts of hydrogen in
loric acid; hence *mercuricum*, Hg″ (or the mercury in mercuric
diatomic.
following table exhibits the formulæ of some of the chief com-
of mercury on the three views :—

	Equiv. Formula, Hg = 100.	Atomic Formula, Hg = 100 = 1 vol.	Atomic Formula, Hg = 200 = 2 vols.
rous oxide,	$Hg_2O = 208$	$Hg_4\Theta = 416$	$Hg_2\Theta = 416$
ric oxide,	$HgO = 108$	$Hg_2\Theta = 216$	$Hg\Theta = 216$
el, .	$Hg_2Cl = 235{\cdot}5$	$Hg_2Cl = 235{\cdot}5$ = 2 vols.	$HgCl = 235{\cdot}5$ = 2 vols.
ive sub-te,	$HgCl = 135{\cdot}5$	$HgCl_2 = 271$ vols.	$HgCl_2 = 271$ = 2 vols.
rous sul-le, . .	$Hg_2S =$		$Hg_2S = 432$
lion, .	$HgS =$		$HgS = 232$ = 3 vols.
precipi-te, . .	NH_2I =		$I_2Hg''Cl$ = 251·5

BISMUTH.

275. Bismuth, though useful in various forms of combination, brittle to be employed in the pure metallic state. It is readily guished from other metals by its peculiar reddish lustre and its crystalline structure, which is very perceptible upon a freshly surface; large cubical (or, strictly speaking, rhombohedral) crys bismuth are easily obtained by melting a few ounces in a crucible, ing it to cool till a crust has formed upon the surface, and pour the portion which has not yet solidified, when the crystals are found the interior of the crucible. It is somewhat lighter than lead (sp. g and volatilises more readily at high temperatures.

Unlike most other metals, bismuth is found chiefly in the metallic disseminated, in veins, through gneiss and clay-slate. The chief is derived from the mines of Schneeberg, in Saxony, where it is ass with the ores of cobalt.

In order to extract the metal from the masses of earthy matter th which it is distributed, advantage is taken of its very low fusing (507° F.) The ore is into small pieces, a troduced into iron cy which are fixed in clined position over nace (fig. 254). The opening of the cyl through which the o troduced, is provide an iron door, and th opening is closed plate of fire-brick per for the escape of the which flows out wh

Fig. 254.—Extraction of bismuth.

cylinders are heated, into iron receiving pots, which are kept h charcoal fire.

Commercial bismuth generally contains considerable quantities of sulphur, and silver; it is sometimes *cupelled* in the same manner in order to extract the silver, the oxide of bismuth being afterwar reduced to the metallic state by heating it with charcoal. Pure dissolves entirely and easily in diluted nitric acid (sp. gr. 1·2); b contains arsenic, a white deposit of arseniate of bismuth is obtained. chloric and diluted sulphuric acids will not act upon bismuth.

The chief use of bismuth is in the preparation of certain allo other metals. Some kinds of type metal and stereotype metal bismuth, which confers upon them the property of expanding mould during solidification, so that they are forced into the finest the impression.

This metal is also remarkable for its tendency to lower the fusi of alloys, which cannot be accounted for merely by referring to fusing point of the metal itself. Thus, an alloy of 2 parts b 1 part lead, and 1 part tin, fuses below the temperature of boilin although the most fusible of the three metals, tin, requires a tem of 442° F. Bismuth is also employed, together with antimony, in struction of thermo-electric piles.

276. *Oxides of bismuth.*—Three compounds of bismuth with oxygen have been prepared; bismuthous oxide BiO_2, bismuthic oxide BiO_3, and bismuthic acid BiO_5.

Bismuthous oxide (BiO_2) is obtained as a black precipitate by reducing terchloride of bismuth with protochloride of tin in the presence of an excess of potash. It is easily converted into bismuthic oxide when heated in contact with air.

Bismuthic oxide, or teroxide of bismuth (BiO_3), is the basic and most important oxide of the metal. It is formed when bismuth is heated in air, or when nitrate of bismuth is decomposed by heat, and is a yellow powder which becomes brown when heated, and fuses easily. Bismuthic oxide forms the rare mineral *bismuthochre*.

Bismuthic acid (BiO_5) is formed when teroxide of bismuth is suspended in a strong solution of potash through which chlorine is passed, when a red solution of bismuthate of potash is obtained, and hydrated bismuthic acid ($HO . BiO_5$) is precipitated as a red powder, which becomes brown and anhydrous at 270° F. It is easily decomposed by heat, evolving oxygen and leaving $BiO_3 . BiO_5$. When heated with acids it also evolves oxygen, and forms salts of bismuthic oxide. The bismuthates of the alkalies are very unstable, being decomposed by water.

277. The only two salts of bismuth which are known in the arts are the *basic nitrate* (*trisnitrate of bismuth* or *flake-white*) and the *oxychloride of bismuth* (*pearl-white*). The preparation of these compounds illustrates one of the characteristic properties of the salts of bismuth, viz., the facility with which they are decomposed by water with the production of insoluble basic salts.

If bismuth be dissolved in nitric acid, it acquires oxygen from the latter, and becomes teroxide of bismuth, which combines with nitric acid to form the nitrate of bismuth ($BiO_3 . 3NO_5$), and this may be obtained in prismatic crystals of the composition $BiO_3 . 3NO_5 + 10Aq$. If the solution be mixed with a large quantity of water, it deposits a precipitate of *flake-white* ($BiO_3 . NO_5 + HO$), or basic nitrate of bismuth, the remainder of the nitric acid being left in the solution.

Pearl-white has the composition $BiCl_3 . 2BiO_3 + HO$, and is obtained by dissolving bismuth in nitric acid, and pouring the solution into water in which common salt has been dissolved.

Terchloride of bismuth ($BiCl_3$) may be distilled over when bismuth is heated in a current of dry chlorine; it is a deliquescent fusible solid, easily dissolved by hydrochloric acid, but decomposed by water, with formation of the above-mentioned *oxychloride of bismuth*; $3BiCl_3 + 6HO = BiCl_3 . 2BiO_3 + 6HCl$. This compound is so insoluble in water that nearly every trace of bismuth may be precipitated from a moderately acid solution of the terchloride by adding much water.

Bismuthous sulphide (BiS_2) is sometimes found in nature, but more frequently *bismuthic sulphide* (BiS_3) or *bismuth glance*, which occurs in dark-grey lustrous prisms isomorphous with native sulphide of antimony. It is also obtained as a black precipitate by the action of hydrosulphuric acid upon bismuthic salts. Bismuthic sulphide is not soluble in diluted sulphuric or hydrochloric acid, but dissolves easily in nitric acid.

278. *Equivalent and atomic weights of bismuth.*—The analysis of the chloride of bismuth has shown it to contain 35·5 parts by weight (1 equivalent) of chlorine combined with 70 parts of bismuth; but the very marked analogy which exists between this chloride and the terchloride of antimony has led to the belief that it is also a terchloride, containing 3 equivalents of chlorine combined with one equivalent (210 parts) of bismuth, and the assumption of the number 210 for the equivalent of bismuth, will be found to receive confirmation from the general analogies of this metal with antimony and arsenic. The specific heat of bismuth confirms the co[illegible] drawn from the composition of the chloride, that the *atomic weight* of identical with its equivalent, or 210, and that this element is t[illegible] nitrogen, phosphorus, and arsenic among the non-metals. The [illegible] for bismuthic oxide is Bi_2O_3; bismuthic chloride, $BiCl_3$; bism[illegible] Bi_2S_3.

ANTIMONY.

279. Antimony is nearly allied to bismuth in both its physical and chemical characters. It is even harder and more brittle than that metal, being easily reduced to a black powder. Its highly crystalline structure is another very well-marked feature, and is at once perceived upon the surface of an ingot of antimony, where it is exhibited in beautiful fern-like markings (*star antimony*). Its crystals belong to the same system (the rhombohedral) as those of bismuth and arsenic. It is much lighter than bismuth (sp. gr. 6·715), and requires a higher temperature (800° F.) to fuse it, though it is more easily converted into vapour, so that, when strongly heated in air, it emits a thick white smoke, the vapour being oxidised. Like bismuth, it is but little affected by hydrochloric or dilute sulphuric acid, but nitric acid oxidises it, though it dissolves very little of the metal, the greater part being left in the form of antimonic acid. The best mode of dissolving antimony is to boil it with hydrochloric acid and to add nitric acid by degrees.

Antimony is chiefly found in nature as *grey antimony ore* or sulphide of antimony (SbS_3), which occurs in Cornwall, but much more abundantly in Hungary. It is found in veins associated with galena, iron pyrites, quartz, and heavy spar. In order to purify it from these, advantage is taken of its easy fusibility, the ore being heated upon the hearth of a reverberatory furnace, with some charcoal to prevent oxidation, when the sulphide of antimony melts and collects below the impurities, whence it is run off and cast into moulds. The product thus obtained is known in commerce as *crude antimony*, and contains sulphides of arsenic, iron, and lead.

To obtain *regulus of antimony* or metallic antimony, the sulphide of antimony is sometimes fused in contact with refuse metallic iron (such as the clippings of tin-plate), when sulphide of iron is formed, and collects as a fused slag upon the surface of the melted antimony—

$$SbS_3 + Fe_3 = 3FeS + Sb .$$

The antimony thus obtained always contains a considerable proportion of iron.

A purer product is procured by another process, which consists in roasting the sulphide in a reverberatory furnace at a temperature insufficient to fuse it, for about twelve hours, when most of the sulphur and arsenic are expelled as sulphurous and arsenious acids, carrying with them a considerable quantity of oxide of antimony. The roasted ore has a brown-red colour, and contains both oxide and sulphide of antimony: it is mixed into a paste with ½ its weight of charcoal saturated with a strong solution of carbonate of soda. The mixture is strongly heated in crucibles, when the oxide of antimony is reduced by the charcoal, and a portion of the sulphide, having been converted into oxide by double decomposition with the soda ($SbS_3 + 3NaO = SbO_3 + 3NaS$), is also reduced, the remainder of the sulphide combining with the sulphide of sodium to form a slag which floats above the metallic antimony; the latter is cast into ingots for the market, and the slag, known as *crocus of antimony* (chiefly $3NaS . SbS_3$), is employed for the preparation of some of the compounds of the metal.

On the small scale, antimony may be extracted from the sulphide by fusing it in an earthen crucible with 4 parts of commercial cyanide of potassium, at a moderate heat; or by mixing 4 parts of the sulphide with 3 of bitartrate of potash and 1½ of

, and throwing the mixture, by small portions, into a red-hot crucible, when ulphur is oxidised and converted into sulphate of potash by the nitre, which is present in sufficient quantity to oxidise the antimony, so that the metal collects e bottom of the crucible.

he brittleness of antimony renders it useless in the metallic state ex- for the construction of thermo-electric piles, where it is employed in unction with bismuth. Antimony is employed, however, to harden ral useful alloys, such as type-metal, shrapnel-shell bullets, Britannia al, and pewter.

morphous antimony.—The ordinary crystalline form of antimony may be obtained, copper and other metals, by decomposing solutions containing the metal by smitting the galvanic current; but in some cases the antimony is deposited from strong solutions in an amorphous condition, having properties very different those of ordinary antimony. The best mode of obtaining it in this form is to mpose a solution of 1 part of tartar emetic (tartrate of antimony and potash) in rts of a strong solution of terchloride of antimony (obtained by heating hydro- ic acid with sulphide of antimony till it refuses to dissolve any more), by the f three cells of Smee's battery, the zinc of which is connected by a copper wire a plate of copper immersed in the antimonial solution, whilst the platinised r of the battery is connected with a plate of antimony in the same solution, at little distance from the copper plate. The deposit of antimony which forms the copper has a brilliant metallic appearance, but is amorphous, and not crys- ne, like the ordinary metal. If it be gently heated or sharply struck, its tem- ture suddenly rises to about 400°, and it becomes converted into a form more ly resembling crystalline antimony. At the same time, however, thick fumes of loride of antimony are evolved, for this substance is always present in the amor- us antimony to the amount of 5 or 6 per cent.,* so that, as yet, there is not suffi- t evidence to establish beyond a doubt the existence of a pure amorphous form ntimony corresponding to amorphous phosphorous, however probable this may ar from the chemical resemblance between these elements.

80. *Oxides of antimony.*—There are two well-known oxides of anti- y, the teroxide (SbO_3) and antimonic acid (SbO_5). *Teroxide* or *sesqui- le of antimony*, or *antimonic oxide*, is formed when antimony burns in and is prepared on a large scale by roasting either the metal or the hide in air, for use in painting as a substitute for white lead. It is found in nature as *white antimony ore* or *valentinite*. Antimonic le forms a crystalline powder usually composed of minute prisms having shape of the rarer form of arsenious acid (p. 251), whilst occasionally s obtained in crystals similar to those of the common octahedral nious acid, with which, therefore, antimonic oxide is *isodimorphous*.† en heated in air it assumes a yellow colour, afterwards takes fire, ulders, and becomes converted into the antimoniate of teroxide of mony ($SbO_3 . SbO_5 = SbO_4$), which was formerly regarded as an inde- dent oxide. The teroxide is insoluble in water, but acids dissolve it, ning salts, though its basic properties are weak, and its salts rather ill ned. Potash and soda are also capable of dissolving it, whence it is etimes called *antimonious acid*.‡

ntimonic acid (SbO_5) is formed when antimony is oxidised with nitric ; it then forms a white powder, which should be well washed and d. When heated it becomes pale yellow, and is decomposed at a high

It has been plausibly suggested that the sudden rise of temperature may be due to presence of an antimony compound analogous to the so-called chloride of nitrogen, the r element being connected with antimony by several chemical analogies.

The octahedral form appears to be produced only when the prismatic for- med in a non-oxidising atmosphere. The mineral *exitèle* is prismatic ox y, and *senarmontite* is the octahedral form of that oxide.

Two crystallised *antimonites of soda* have been obtained, the neut $. SbO_3 + 6Aq.$, *and the terantimonite* $NaO . 3SbO_3 + 2Aq.$; the for *le, the latter almost insoluble in water.*

temperature, leaving $SbO_3 . SbO_5$. It is dissolved by solution of forming antimoniate of potash.

A better method of obtaining the antimoniate of potash co gradually adding 1 part of powdered antimony to 4 parts of nitre a clay crucible, when the oxygen of the nitre converts the antim antimonic acid, which combines with the potash. The mass is p and washed with warm water to remove the excess of nitre and th of potash, when the insoluble anhydrous antimoniate of potas and on boiling this for an hour or two with water, it becomes and dissolves. The solution, when evaporated, leaves a gummy *antimoniate of potash*, having the composition $KO . SbO_5 + 5Aq$

When the solution of antimoniate of potash is treated with acid, a crystalline precipitate of biantimoniate of potash ($KO . 2$ obtained. If antimoniate of potash be fused (in a silver crucil hydrate of potash, it becomes converted into *metantimoniate o* ($2KO . SbO_5$), which is decomposed by water into potash and *timoniate of potash* ($KO . HO . SbO_5$), which may be crystallised solution. This latter salt is valuable as a test for soda, since the timoniate of soda, $NaO . HO . SbO_5$, is one of the very few salts which are insoluble in water, and is therefore obtained as a cr precipitate when the bimetantimoniate of potash is added to a containing soda. The solution of bimetantimoniate of potash is g changed by keeping, into antimoniate of potash ($KO . SbO_5$), wh not so readily precipitate soda.

It will be remarked that the antimoniates correspond in con with the monobasic (or meta) phosphates, whilst the metanti represent the bibasic (or pyro) phosphates.

Naples yellow is a compound of antimonic acid with oxide of l

281. *Antimonietted hydrogen* (SbH_3?) is obtained, mixed with fr gen, when an alloy of zinc and antimony is acted on by diluted acid, or when a solution of a salt of antimony (tartar emetic, for is poured into a hydrogen apparatus containing zinc and dilute acid (fig. 255). If the gas be inflamed as it issues into the air with a livid flame, emitting fumes of antimor and when a piece of glass or porcelain is de the flame (fig. 256) it becomes coated with film of metallic antimony. A red heat decom gas into its elements, so that if the tube throu it is passing be heated with a spirit lamp (fi lustrous black deposit of antimony will be fo beyond the heated part. The composition monietted hydrogen is not certainly establis it has never been obtained unmixed with h but it is believed to contain SbH_3, becau passed into nitrate of silver, it gives a black precipitate containi It would then be analogous to ammonia (NH_3), phosphuretted (PH_3), and arseni quantities of anti by converting it i

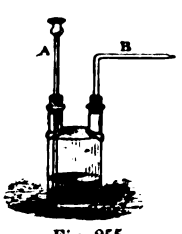


Fig. 255.

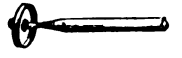


Fig. 256.

282. CHLORIDE mony combine rea

chlorides are among the most im

loride or *sesquichloride of antimony* ($SbCl_3$) may be prepared by
g 3 parts of powdered antimony with
of corrosive sublimate, when calomel
amalgam of antimony are left, and
hloride of antimony (boiling at 433°
ils over—

Fig. 257.

$$3HgCl = SbCl_3 + SbHg_2 + Hg_2Cl.$$

lso be obtained by boiling powdered
y or sulphide of antimony to dry-
th strong sulphuric acid, and distil-
sulphate of teroxide of antimony
tained, with common salt. The ter-
is a soft grey crystalline fusible
hence its old name of *butter of anti-*

It may be dissolved in a small quantity of water, but a large
y of water decomposes it, forming a bulky white precipitate, which
ychloride of antimony ($3SbCl_3 + 6HO = SbCl_3.2SbO_3 + 6HCl$).
hot water is added to a hot solution of terchloride of antimony in
loric acid, minute prismatic needles are deposited, containing
$5SbO_3$, and formerly called *powder of Algaroth*. The terchloride
nony, in its behaviour with water, much resembles that of bismuth.
ride of antimony is occasionally used in surgery as a caustic; it also
as a bronze for gun-barrels, upon which it deposits a film of
ay.

achloride of antimony ($SbCl_5$) is prepared by heating coarsely
ed antimony in a retort, through which a stream of dry chlorine is
(fig. 199), the neck of the retort being fitted into an adapter, which
o condense the pentachloride. One ounce of antimony will require
orine from about 6 oz. of common manganese and 18 oz. (measured)
rochloric acid. The pure pentachloride is a colourless fuming
of a very suffocating odour; it combines energetically with a small
y of water, forming a crystalline hydrate, but an excess of water
oses it into hydrochloric and hydrated metantimonic acids, the
orming a white precipitate—

$$SbCl_5 + 7HO = 5HCl + 2HO.SbO_5.$$

hloride of antimony is employed by the chemist as a chlorinating
thus, olefiant gas (C_4H_4) when passed through it, is converted into
liquid ($C_4H_4Cl_2$), and carbonic oxide into phosgene gas, the penta-
e of antimony being converted into terchloride.

pentachloride of antimony is the analogue of pentachloride of
orus, and a *chlorosulphide of antimony* ($SbCl_3S_2$), corresponding to
ulphide of phosphorus, is obtained as a white crystalline solid by
ion of hydrosulphuric acid upon pentachloride of antimony.

he *tersulphide* or *sesquisulphide* of
the chief ore of antimony. It is a
k-grey colour and metallic lustre,
long prismatic needles. It fuses
out of contact with air. It is
with hydrochloric acid, when
and if the solution be poured

into water, it deposits an orange precipitate. This orange sulphide, has the same composition as the grey sulphide, is also obtained by hydrosulphuric acid to a solution of a salt of antimony (for example, emetic) acidulated with hydrochloric acid. It may be converted i grey sulphide by the action of heat. The orange variety constitu *antimony vermilion*, the preparation of which has been described at Native tersulphide of antimony is employed, in conjunction with c of potash, in the *friction-tube* for firing cannon; it is also used *cussion caps*, together with chlorate of potash and fulminate of m Its property of deflagrating with a bluish-white flame when heate nitre renders it useful in compositions for coloured fires.

Glass of antimony is a transparent red mass obtained by roasti tersulphide of antimony in air, and fusing the product; it contain 8 parts of teroxide and 1 part of tersulphide of antimony.

Red antimony ore is an oxysulphide of antimony, $SbO_3 . 2SbS_3$

Pentasulphide of antimony (SbS_5) is obtained as a bright ora precipitate by the action of hydrosulphuric acid upon a solution of chloride of antimony in hydrochloric acid.

Both the sulphides of antimony are sulphur-acids, capable of com with the alkaline sulphides to form *sulphantimonites* and *sulphantim* respectively. Hence they are easily dissolved by alkalies and a sulphides. Even metallic antimony, in powder, is dissolved when heated with solution of sulphide of potassium, in which sulphur ha dissolved, any lead or iron which may be present being left in the r so that the antimony may be tested by this process as to its freedo those metals.

Mineral kermes is a variable mixture of teroxide and tersulpl antimony, which is deposited as a reddish-brown powder from the s obtained by boiling tersulphide of antimony with potash or soda. formerly much valued for medicinal purposes.

Schlippe's salt is the sulphantimoniate of sulphide of (3NaS, SbS_5, 18HO) and may be obtained in fine transparent tetr crystals.

284. *Equivalent and atomic weights of antimony.*—The solid chl antimony (terchloride) has been found to contain 35·5 parts by (1 eq.) of chlorine, combined with 40·66 parts of antimony, so that chloride be assumed to contain 1 equivalent of antimony, combin one of chlorine, the equivalent weight of the metal would be 40·66 upon this supposition, the liquid (penta-)chloride would contai of antimony and $1\frac{2}{3}$ eq. of chlorine, whilst the analogy of this with pentachloride of phosphorus shows that it must contain 5 chlorine, and that the solid chloride must contain 3 eqs. of chlori bined with 1 eq. of antimony; hence, the equivalent weight of a is 122.

The specific heat of antimony, and its isomorphism with arseni that its *atomic weight* is identical with its equivalent, so that it acts the part of a triatomic element, occupying the place of thre of hydrogen.

The weight of 1 volume, or specific gravity, of the vapour of ter of antimony, has been found to be 8·1. Assuming it to have a constitution, and to contain, in 2 volumes, 1 vol. of antimony vap vols. of chlorine, the specific gravity of vapour of antimony would

Weight of 2 vols. vapour of $SbCl_3$, - -	16·20
„ 3 vols. chlorine, - - -	7·41
„ 1 vol. of antimony vapour, -	8·79

weight of 1 vol. of antimony vapour, therefore, would be rather more
a 122 times that of 1 vol. of hydrogen, so that this number may be
pted as the atomic weight of the metal. The *atomic formulæ* of
e of the chief compounds of antimony are—antimonic oxide, Sb_2O_5;
monic acid, Sb_2O_5; sulphantimonious acid, Sb_2S_3; sulphantimonic
, Sb_2S_5; terchloride of antimony, $SbCl_3$; pentachloride, $SbCl_5$.
he equivalent of antimony was formerly taken at half its present value,
nce the names of sesquichloride, &c., instead of terchloride, &c.

TIN.

285. Tin is by no means so widely diffused as most of the other metals
ich are largely used, and is scarcely ever found in the metallic state in
ure. Its only important ore is that known as *tin-stone*, which is a
oxide of tin (SnO_2), and is generally found in veins traversing quartz,
nite, or slate. It is generally associated with arsenical iron pyrites,
with a mineral called *wolfram*, which is a compound of tungstic acid
O_3) with the oxides of iron and manganese.

Tin-stone is sometimes found in alluvial soils in the form of detached
nded masses; it is then called *stream tin ore*, and is much purer than
t found in veins, for it has undergone a natural process of oxidation
l levigation exactly similar to the artificial treatment of the impure ore.
ese detached masses of stream tin ore are not unfrequently rectangular
sms with pyramidal terminations.

The Cornish mines furnish the largest supplies of tin, and those of
alacca and Banca stand next. At the Cornish tin-works the purer
rtions of the ore are picked out by hand, and the residue, which contains
uartz and other earthy impurities, together with copper pyrites and
senical iron pyrites, is reduced to a coarse powder in the stamping-mills,
d washed in a stream of water. The tin-stone, being extremely hard,
not reduced to so fine a powder as the pyritous minerals associated with
, and these latter are therefore more readily carried away by the stream
f water than the tin-stone. The removal of the foreign matters from the
re is also much favoured by the high specific gravity of the binoxide of
in, which is 6·5, whilst that of sand or quartz is only 2·7, so that the
tter would be carried off by a stream which would not disturb the former.
o easily and completely can this separation be effected, that a sand con-
aining less than one per cent. of tin-stone is found capable of being
conomically treated.

In order to expel any arsenic and sulphur which may still remain in
he washed ore, it is roasted in quantities of 8 or 10 cwts. in a reverbera-
ory furnace, when the sulphur is disengaged in the form of sulphurous
cid, and the arsenic in that of arsenious acid, the iron left in the
tate of sesquioxide, and the copper partly as sulphate partly
s unaltered sulphide. To complete the oxidation of th hide
f copper, and its conversion into the soluble sulpha is
noistened with water and exposed to the air for so
he whole of the copper may be removed by again w

A second washing in a stream of water also removes the sesquio iron in a state of suspension, and this is much more easily effecte when the iron was in the form of pyrites, since the difference betwe specific gravity of this mineral (5·0) and that of the tin-stone (6·5 less than that between sesquioxide of iron and tin-stone.

The ore thus purified contains between 60 and 70 per cent. of is mixed very intimately with about $\frac{1}{8}$ of powdered coal, and a litt or fluor spar to form a fusible slag with the earthy impurities; the m is sprinkled with water to prevent its dispersion by the draught and thrown on the hearth (A, fig. 258) of a reverberatory furn charges of between 20 and 25 cwts.

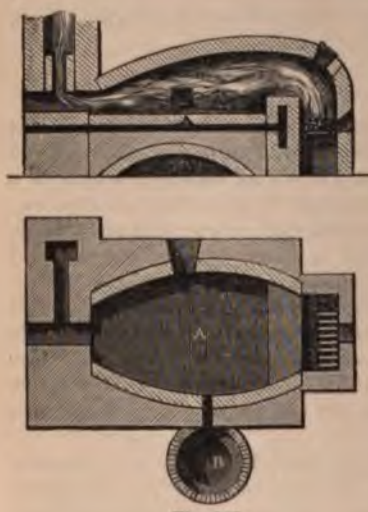


Fig. 258.

The temperature is not per to rise too high at first, lest a p of the oxide of tin should c with the silicic acid to form cate, from which the metal be reduced with difficulty.

During the first 6 or 8 ho doors of the furnace are kep so as to exclude the air and the reducing action of the upon the binoxide of tin, th gen of which it converts in bonic oxide, leaving the tin metallic state to accumulate the hearth beneath the layer When the reduction is deeme plete, the mass is well stirre an iron paddle to separate th from the slag; the latter is r first, and the tin is then dr into an iron pan (B), wher allowed to remain at rest dross to rise to the surface, and is ladled out into ingot-moulds.

The slags drawn out of the smelting-furnace are carefully sorted which contain much oxide of tin being worked up with the next ch ore, whilst those in which globules of metallic tin are dissemina crushed, so that the metal may be separated by washing in a st water.

The tin, when first extracted from the ore, is far from pure, bei taminated with small quantities of iron, arsenic, copper, and tu In order to purify it from these, the ingots are piled into a hollo near the fire-bridge of a reverberatory furnace, and gradually heated fusing point, when the greater portion of the tin flows into an outer whilst the remainder is converted into the binoxide, which rem dross upon the hearth, together with the oxides of iron, copper, an sten, the arsenic having passed off in the form of arsenious acid. ingots of tin are introduced at intervals, until about 5 tons of th have collected in the basin, which is commonly the case in about after the commencement of the operation.

The specific gravity of tin being very low (7·285), any dross may still remain mingled with it does not separate very read obviate this, the molten metal is well agitated by stirring, w

den poles, or lowering billets of wet wood into it, when the evolved bles of steam carry the impurities up to the surface in a kind of froth; stirring is continued for about three hours, and the metal is allowed to ain at rest for two hours, when it is skimmed and ladled into ingot-lds. It is found that, in consequence of the lightness of the metal, its tendency to separate from the other metals with which it is con-inated, the ingots which are cast from the metal first ladled out of the are purer than those from the bottom; this is shown by striking the ingots with a hammer, when they break up into the irregular prismatic ments known as *dropped* or *grain-tin*, the impure metal not exhibiting extreme brittleness at a high temperature. The tin imported from ca is celebrated for its purity (*Straits tin*).

When the tin ore contains wolfram, it is usual to purify it before smelt-, by fusion with carbonate of soda in a reverberatory furnace, when tungstic acid is converted into tungstate of soda, which is dissolved by water and crystallised. This salt finds an application in calico-ting.

n the small scale, tin may be extracted from tin-stone, by fusing 100 ns with 20 grains of dried carbonate of soda, and 20 of dried borax, crucible lined with charcoal, exactly as in the extraction of iron p. 321).

86. By its physical characters, tin is very readily distinguished from r metals. If a bar of tin be bent, it emits a peculiar crackling sound. h the exception of lead and zinc, it is the least tenacious of all the als in common use; its ductility is therefore very low, and lead is the common metal which is more difficult to draw into wire at the nary temperature. Tin may, however, be drawn at 212° F.

n fusibility, tin surpasses all the other common metals, becoming liquid 442° F., but it is not easily vaporised. Its malleability is also very t, only gold, silver, and copper exhibiting this quality in a higher ree. This malleability is shown in the manufacture of *tin-foil*, where tes of the best tin are hammered down to a certain thinness, then cut laid upon each other, and again beaten till extended to the required ree.

Tin-plate, it must be remembered, is made in a very different way, by ting sheets of iron with a layer of tin; the best kind, known as *block* being that which is covered with the thickest layer of tin, and after-ds hammered upon a polished anvil in order to consolidate the coating make it adhere more firmly. Tin, being unaltered by exposure to air he ordinary temperature, will effectually protect the iron from rust as g as the coating of tin is perfect, but as soon as a portion of the tin is oved so as to leave the iron exposed, corrosion will take place very idly, because the two metals form a galvanic couple, which will decom-e the water (charged with carbonic acid) deposited upon them from air, and the iron, having the greater attraction for oxygen, will be the al attacked. In the case of galva coated with zinc), on the trary, the zinc would be the m d hence the greater ability of this material under cer

or the manufacture of tin-plate ned with char- (*see* p. 310) is employed, and t of the process sists in cleansing the iron plates which would *ent the adhesion of the tin.* T to undergo

several processes, of which the most important are—(1), immer diluted sulphuric acid; (2), heating to redness; (3), hammering ar ing to scale off the oxide; (4), steeping in sour bran; (5), immer mixed diluted sulphuric and hydrochloric acids; (6), scouring with (7), washing with water; they are then dried for an hour in a v melted tallow which prevents contact of air, and immersed for a and a half in melted tin, the surface of which is protected from ox by tallow; after draining, they are dipped a second time into the thicken the layer; then transferred to a bath of hot tallow to all superfluous tin to run down to the lower edge, whence it is afte removed by liquefying it in a vessel of melted tin, and shaking it sharp blow. About 8 lbs. of tin are required to cover 225 plates, ing 112 lbs.

Terne-plate is iron coated with an alloy of tin and lead. In t the interior of copper vessels, in order to prevent the contamina food with the metal, the surface is first thoroughly cleaned from by heating it and rubbing over it a little sal-ammoniac (hydroc of ammonia, NH_3. HCl), which decomposes any oxide of coppe verting it into the volatile chloride of copper ($CuO + NH_3$. H $CuCl + HO + NH_3$). A little resin is then sprinkled upon the s surface, to protect it from oxidation, and the melted tin is spre it with tow.

Pins (made of brass wire) are coated with tin by boiling the cream of tartar (bitartrate of potash), common salt, alum, granula and water; the tin is oxidised at the expense of the water, and dissolved by the acid liquid, from which solution it is reduced action of the zinc in the brass, for zinc is more highly electro-positi tin, and is therefore capable of precipitating the metal from its sol

287. *Alloys of tin.*—The solder employed for tin wares is an tin and lead in various proportions, sometimes containing 2 part to 1 of lead (fine solder), sometimes equal weights of the two (common solder), and sometimes 2 parts of lead to 1 of tin (coarse All these alloys melt at a lower temperature than tin, and, therefo lead. In applying solder, it is essential that the surfaces to be u quite free from oxide, which would prevent the adhesion of the this is insured by the application of sal-ammoniac, or of hydr acid,* or sometimes of powdered borax, remarkable for its ready f and its solvent power for the metallic oxides.

Tin forms the chief part of the alloys known as pewter and I metal, the former being composed of about 4 parts of tin and 1 whilst the latter contains, in addition to the tin, comparative quantities of antimony, copper, and lead. Another similar alloy posed of 12 parts of tin, 1 of antimony, and a little copper.

Gun metal is an alloy of 90·5 parts of copper with 9·5 of tin, e valuable for its tenacity, hardness, and fusibility. In prepa alloy, it is usual to melt the tin, in the first place, with twice it of copper, when a white, hard, and extremely brittle alloy (*hard* obtained. The remainder of the copper is fused in a deoxidis on the hearth of a reverberatory furnace, and the hard metal th mixed with it, long wooden stirrers being employed. A quanti

* It is customary to *kill* the hydrochloric acid by dissolving some zinc i chloride of zinc is probably useful in protecting the work from oxidation.

gun metal is usually melted with the copper, and facilitates the mixing of the metals. When the metals are thoroughly mixed, the oxide is removed from the surface, and the gun metal is run into moulds made of sand, the stirring being continued during the running, in order to prevent the separation, to which this alloy is very liable, of a white alloy containing a larger proportion of tin, which has a lower specific gravity, and would chiefly collect in the upper part of the casting. In casting cannon (erroneously called *brass* guns), the mould is placed perpendicularly with the muzzle upwards, the upper part of the mould being about 3 feet longer than is required for the gun, so that a superfluous cylinder of metal or *dead-head* is formed, in which the separated alloy collects, together with any oxide or dross which may have run out with the metal; probably, also, the weight of this column of metal hastens the solidification and hinders the separation of the metals, at the same time increasing the density and consequent tenacity of the metal at the breech of the gun; this dead-head is cut off before the gun is turned and bored. The metal is run into the mould at a temperature as near its point of solidification as possible, so as to diminish the chance of separation. The purest commercial qualities of copper and tin are always employed in gun metal.

Bronze is essentially an alloy of copper and tin, containing more tin than gun metal; its composition is varied according to its application, small quantities of zinc and lead being often added to it. Bronze is affected by changes of temperature, in a manner precisely the reverse of that in which steel is influenced, for it becomes hard and brittle when allowed to cool slowly, but soft and malleable when quickly cooled. The art of making bronze was practised before any progress had been made in working iron, and ancient weapons were very commonly of this material.

Bronze coin (substituted for the copper coinage) is composed of 95 copper, 4 tin, and 1 zinc.

Bell metal is an alloy of about 4 parts of copper and 1 of tin, to which lead and zinc are sometimes added. The metal of which musical instruments are made generally contains the same proportions of copper and tin as bell metal.

Speculum metal, employed for reflectors in optical instruments, consists of 2 parts of copper and 1 of tin, to which a little zinc, arsenic, and silver are sometimes added to harden it and render it susceptible of a high polish.

A superior kind of *type metal* is composed of 1 part of tin, 1 of antimony, and 2 of lead.

Tin is not dissolved by nitric acid, but is converted into a white powder, the binoxide of tin; hydrochloric acid dissolves it with the aid of heat, evolving hydrogen; but the best solvent for tin is a mixture of hydrochloric with a little nitric acid. When the metal is acted upon by hydrochloric acid, it assumes a crystalline appearance, which has been turned to account for ornamenting tin-plate. of common tin-plate be rubbed over with tow dipped in a w f hydrochloric and nitric acids, its surface is very prettily *métallique*); it is usual to cover the surface with a colou sh.

Commercial tin is liable to contain mi . iron, copper, arsenic, *antimony*, *bismuth*, *gold* gsten. *Pure tin may be precipitated in crystals* rrent

excited by immersing a plate of tin in a strong solution of stan chloride, covered with a layer of water, so that the metal may be in c tact with both layers of liquid.

288. OXIDES OF TIN.—Two oxides of this metal are known—the p oxide, SnO, and the binoxide, SnO_2.

Protoxide of tin (SnO), or *stannous oxide*, is a substance of little p tical importance, obtained by decomposing stannous chloride wit alkali. Its colour varies, according to the mode of preparing it, f black or olive-coloured to red. It is a feebly basic oxide, and the dissolves in the acids; it may also be dissolved by a strong solutio potash, but is then easily decomposed into metallic tin and the bin which combines with the potash.

Binoxide of tin (SnO_2), or *stannic oxide*, has been mentioned as chief ore of tin, and is formed when tin is heated in air. *Tin-ston cassiterite*, as the natural form of this oxide is called, occurs in very l square prisms, usually coloured brown by peroxide of iron. In its in bility in acids it resembles crystallised silica, and, like that substanc forms, when fused with alkalies or their carbonates, compounds which soluble in water; these compounds are termed *stannates*, the binoxide tin being known as *stannic acid*.

Stannate of soda is prepared, on the large scale, for use as a mord by calico-printers. The prepared tin ore (p. 384) is heated with soluti of hydrate of soda, and boiled down till the temperature rises to 500° 600° F.; or the tin ore is fused with nitrate of soda, when the nitric a is expelled. It crystallises easily in hexagonal tables having the comp sition $NaO . SnO_2$, 4Aq., which dissolve easily in cold water, and a partly deposited again when the solution is heated. Most neutral salts o the alkalies also cause a separation of stannate of soda from its aqueou solution. The solution of stannate of soda has, like the silicate, a strong alkaline reaction, and when neutralised by an acid, yields a precipitate of hydrated stannic acid, $HO . SnO_2$. If the solution of stannate of soda be added to an excess of hydrochloric acid, the stannic acid remains in solu tion, and if the liquid be dialysed (*see* p. 104), a jelly is first formed, which gradually liquefies as the chloride of sodium diffuses away, and eventually a pure aqueous solution of stannic acid is obtained, which is very easily gelatinised by the addition of a minute quantity of hydrochloric acid, or of some neutral salt. The great similarity between stannic and silicic acids is here very remarkable. When heated, stannic acid is converted into metastannic acid.

Metastannic acid (Sn_5O_{10}) is obtained as a white crystalline hydrate when tin is oxidised by nitric acid; when washed with water and dried by exposure to air, it has the composition $Sn_5O_{10} . 10HO$, but when dried at 212° F. it becomes $Sn_5O_{10} . 5HO$. If more strongly heated, it assumes a yellowish colour, and a hardness resembling that of powdered tin-stone. *Putty powder*, used for polishing, consists of meta-stannic acid; as found in commerce it generally contains much oxide of lead. Meta-stannic acid is insoluble in water and diluted acids, and when *fused* with hydrated alkalies, is converted into a soluble stannate; but if *boiled* with solution of potash it is dissolved in the form of metastannate of potash, which will not crystallise, like the stannate, but is obtained as a granular precipitate by dissolving hydrate of potash in its solution. This precipitate has the composition $KO . Sn_5O_{10} . 4Aq.$; it is very soluble in water, and is strongly alkaline. When it is heated to expel the water, it is decomposed, and the potash may be washed out with water, leaving meta-nnic acid. The hydrated metastannic acid may be distinguished from hydrated

nic acid by the action of protochloride of tin, which converts it into the yellow stannate of tin ($SnO . Sn_5O_{10} . 4Aq.$)

Stannate of tin is obtained as a yellowish hydrate by boiling protochloride of tin with hydrated sesquioxide of iron; $Fe_2O_3 + 2SnCl = SnO . SnO_2 + 2FeCl$. It is sometimes written Sn_2O_3, and called *sesquioxide of tin.*

289. CHLORIDES OF TIN.—The two chlorides of tin correspond in composition to the oxides.

Stannous chloride, or *protochloride of tin* ($SnCl$), is much used by dyers and calico-printers, and is prepared by dissolving tin in hydrochloric acid, when it is deposited, on cooling, in lustrous prismatic needles ($SnCl . 2Aq.$), known as *tin crystals* or *salts of tin.* The solution of the tin is generally effected in a copper vessel, in order to accelerate the action by forming a voltaic couple, of which the tin is the attacked metal. When gently heated, the crystals lose their water, and are partly decomposed, some hydrochloric acid being evolved ($SnCl + HO = SnO + HCl$); but, at a higher temperature, a great part of the chloride may be distilled in the anhydrous state; the anhydrous chloride is generally prepared by distilling powdered tin with corrosive sublimate, when it remains in the retort as a brilliant grey solid, which requires a bright red heat to convert it into vapour. When water is poured upon the crystals of stannous chloride, they are only partially dissolved, a white oxychloride of tin ($SnCl . SnO . 2Aq.$) being separated. A moderately dilute solution of stannous chloride absorbs oxygen from the air, and deposits a white compound of bichloride and protoxide of tin; $2SnCl + O_2 = SnCl_2 . SnO_2$. If the solution contains much free hydrochloric acid it remains clear, being entirely converted into bichloride of tin. A strong solution of the chloride is not oxidised by the air, and the weak solution may be longer preserved in contact with metallic tin. Stannous chloride has a great attraction for chlorine as well as for oxygen, and is frequently employed as a deoxidising or dechlorinating agent. Tin may be precipitated from stannous chloride by the action of zinc, in the form of minute crystals. A very beautiful *tin tree* is obtained by dissolving granulated tin in strong hydrochloric acid, with the aid of heat, in the proportion of 8 measured oz. of acid to 1000 grs. of tin, diluting the solution with four times its bulk of water, and introducing a piece of zinc.

Stannic chloride, or *bichloride of tin* ($SnCl_2$), is obtained in solution when tin is heated with hydrochloric and nitric acids; for the use of the dyer, the solution is generally made with hydrochlorate of ammonia (sal-ammoniac) and nitric acid (*nitromuriate of tin*). The anhydrous bichloride is obtained by heating tin in a current of dry chlorine, when combination takes place with combustion, and the bichloride distils over as a heavy liquid (sp. gr. 2·28) colourless liquid, volatile (boiling point, 240° F.), and giving suffocating white fumes in the air. When mixed with a little water, energetic combination takes place, and a crystalline hydrate ($SnCl_2 . 5Aq.$) is formed, which is decomposed by an excess of water, with separation of hydrated stannic acid. Stannic chloride forms crystallisable double salts with the alkaline chlorides. *Pink salt*, used by dyers, is a compound of stannic chloride with hydrochlorate of ammonia ($NH_3 . HCl . SnCl_2$).

290. *Sulphides of tin.*—The *protosulphide*, or *stannous sulphide* (SnS), is found in Cornwall as *tin pyrites*, and may be easily formed by heating tin with sulphur, when it forms a grey crystalline mass. It is also obtained as a dark brown precipitate by the action of sulphuretted hydrogen *on a solution of stannous chloride.* Protosulphide of tin

base, but it may be dissolved by alkalies if some sulphur be added, which converts it into the bisulphide, a decided sulphur acid.

Bisulphide of tin, or ***stannic sulphide*** (SnS_2), is commonly known as ***mosaic gold*** or ***bronze powder***, and is used for decorative purposes. It is prepared by a curious process, which was devised in 1771, and must have been the result of a number of trials. 12 parts by weight of tin are dissolved in 6 parts of mercury; the brittle amalgam thus obtained is powdered and mixed with 7 parts of sulphur and 6 of sal-ammoniac. The mixture is introduced into a Florence flask, which is gently heated in a sand-bath as long as any smell of hydrosulphuric acid is evolved; the temperature is then raised to dull redness until no more fumes are disengaged. The mosaic gold is found in beautiful yellow scales at the bottom of the flask, and sulphide of mercury and calomel are deposited in the neck. The mercury appears to be used for effecting the fine division of the tin, and the sal-ammoniac to keep down the temperature (by its volatilisation) below the point at which the bisulphide of tin is converted into protosulphide.

Mosaic gold, like the metal itself, is not dissolved by hydrochloric or nitric acid, but easily by *aqua regia*. Alkalies also dissolve it when heated, since the bisulphide of tin is a sulphur acid. On adding hydrosulphuric acid to a solution of stannic chloride, the stannic sulphide is obtained as a yellow precipitate.

291. *Equivalent and atomic weights of tin.*—When tin is oxidised by nitric acid, 8 parts by weight (1 eq.) of oxygen are taken up by 29·5 parts of the metal, and if the oxide thus formed be composed of single equivalents, 29·5 must be the equivalent weight of tin; but the existence of another oxide, containing only half as much oxygen, and the analogies between the first mentioned oxide and silicic acid (SiO_2), lead to the conclusion that the oxide obtained by the action of nitric acid is a binoxide, containing 16 parts by weight of oxygen, combined with 1 eq. of tin, when the equivalent weight of the metal would be 59.

But the specific heat of tin shows that its *atomic weight* must be represented by the number 118, and this receives confirmation from the specific gravity of the vapour of stannic chloride.

Weight of 1 vol. of stannic chloride vapour, .	9·20
„ 2 vols. (1 molecule), . . .	18·40
„ tin contained in it, . . .	8·35
„ chlorine contained in 2 vols. of stannic chloride, . . .	10·05

Since 2·47 is the specific gravity or weight of 1 vol. of chlorine, the number 10·05 represents 4 vols. of that gas; and if it be allowed that 2 vols. of stannic chloride represent, as usual, 1 molecule, it will contain 1 atom of tin and 4 atoms (or vols.) of chlorine, and its *molecular formula* will be $SnCl_4$ (Sn = 118). Tin, therefore, would be a tetratomic element like carbon and silicon, one atom being capable of occupying the place of four atoms of hydrogen, and the *atomic formulæ* for some of its chief compounds would be—stannous oxide, SnO; stannic acid, SnO_2; stannous chloride, $SnCl_2$; stannic chloride, $SnCl_4$; stannous sulphide, SnS; stannic sulphide, SnS_2.

292. TITANIUM, which stands in close chemical relationship to tin, used to be described as a very rare metal, but it has lately been found to exist in considerable quantity in iron ores and clays, although no very important practical application has hitherto been found for it. The form in which it is generally found is *titanic acid* (TiO_2), which occurs uncombined in the minerals *rutile*, *anatase*, and *brookite*, the first of which is isomorphous with tin-stone, and is extremely hard like that mineral. In combination with oxide of iron, titanic acid is found in *iron-sand*, *kerine*, or *menachanite* (found originally at Menachan in Cornwall), which resembles gunpowder in appearance, and is now imported in abundance from Nova Scotia and New Zealand. Some specimens of this mineral contain 40 per cent. of titanic acid, combined with protoxide of iron. To extract titanic acid from it, the finely ground mineral is fused with three parts of carbonate of potash, when carbonic acid is expelled and titanate of potash formed; on washing the mass with hot water, this salt is decomposed, a part of its alkali being removed by the water, and an acid titanate of potash left, mixed with the oxide of iron. This is dissolved in hydrochloric acid, and the solution evaporated to dryness, when the titanic acid, and any silicic acid which may be present, are converted into the insoluble modifications, and are left on digesting the residue again with dilute hydrochloric acid; the residue is washed with water (by decantation, for titanic acid easily passes through the filter), dried, and fused at a gentle heat with bisulphate of potash. The sulphuric acid forms a soluble compound with the titanic acid ($TiO_2 . SO_3$), which may be extracted by cold water, leaving the silicic acid undissolved. The solution containing the titanic acid is mixed with about twenty times its volume of water, and boiled for some time, when the titanic acid is separated as a white precipitate, exhibiting a great disposition to cling as a film to the surface of the flask in which the solution is boiled, and giving it the appearance of being corroded. The titanic acid becomes yellow when strongly heated, and white again on cooling; it does not dissolve in solution of potash like silica, but when fused with potash it forms a titanate, which is decomposed by water; the acid titanate of potash which is left may be dissolved in hydrochloric acid, and if the solution be neutralised with carbonate of ammonia, hydrated titanic acid is precipitated, very much resembling alumina in appearance. By dissolving the gelatinous hydrate in cold hydrochloric acid, and dialysing, a solution of titanic acid in water is obtained, which is liable to gelatinise spontaneously if it contain more than one per cent. of the acid.

Titanic acid is employed in the manufacture of artificial teeth, and for imparting a straw-yellow tint to the glaze of porcelain.

If a mixture of titanic acid and charcoal be heated to redness in a porcelain tube, through which dry chlorine is passed, *bichloride of titanium* ($TiCl_2$) is obtained as a colourless volatile liquid, very similar to bichloride of tin. By passing the vapour of the bichloride of titanium over heated sodium, the *metallic titanium* is obtained in prismatic crystals resembling specular iron ore in appearance. Like tin, it is said to dissolve in hydrochloric acid with liberation of hydrogen. The most remarkable chemical feature of titanium is its direct attraction for nitrogen, with which it combines when strongly heated in air. By passing ammonia gas over titanic acid heated to redness, a violet powder is formed, which is a nitride of titanium (TiN). Beautiful cubes of a copper colour and great hardness, formerly believed to be metallic titanium, are found adhering to the slags of blast-furnaces in which titaniferous iron ores are smelted; these contain about 77 per cent. of titanium, 18 of nitrogen, and rather less than 4 of carbon, and are believed to consist of a compound of cyanide with nitride of titanium, $TiCy, 3Ti_3N$. A similar compound is obtained by passing nitrogen over a mixture of titanic acid and charcoal heated to whiteness.

Violet-coloured crystals of sesquichloride of titanium (Ti_2Cl_3) are obtained by passing hydrogen charged with vapour of bichloride of titanium through a red-hot porcelain tube; it forms a violet solution in water, which resembles stannous chloride in its reducing properties.

When a solution of titanic acid (or acid titanate of potash) in hydrochloric acid is acted on by zinc, a violet solution is formed, which deposits, after a time, a blue (or green) precipitate, which appears to be a *sesquioxide of titanium* (Ti_2O_3), and rapidly absorbs oxygen from the air, being converted into titanic acid. A *protoxide of titanium* (TiO) is said to be obtained as a black powder when titanic acid is strongly heated in a crucible lined with charcoal.

Bisulphide of titanium is not precipitated, like bisulphide of tin, when hydrosulphuric acid acts upon the bichloride; but if a mixture of the vapour of bichloride

of titanium with hydrosulphuric acid is passed through a red-hot tube, greenish-yellow scales of the bisulphide, resembling mosaic gold, are deposited.

Titanium, like tin, is classed among the tetratomic elements; its equivalent is 25, and its atomic weight 50.

293. TUNGSTEN is chiefly found in the mineral *wolfram*, which occurs, often associated with tin-stone, in large brown shining prismatic crystals, which are very heavier than tin-stone (sp. gr. 7·3), from which circumstance the metal derives its name, tungsten, in Swedish, meaning heavy stone. The symbol (W) used for tungsten is derived from the Latin name *wolframium*. Wolfram contains the tungstates of iron and manganese in somewhat variable proportions, but its general composition is expressed by the formula $MnO.WO_3, 3(FeO.WO_3)$. *Scheelite*, tungstate of lime ($CaO.WO_3$), is another mineral in which tungsten is found.

Tungstate of soda is employed by calico-printers as a mordant, and is sometimes applied to muslin, in order to render it inflammable. It is obtained by fusing wolfram with carbonate of soda, an operation to which tin ores containing this mineral in large quantity are sometimes submitted previously to smelting them. Water extracts the tungstate of soda, which may be crystallised in rhomboidal plates having the composition $NaO.WO_3, 2Aq$. When a solution of this salt is mixed with an excess of hydrochloric acid, white *hydrated tungstic acid* ($HO.WO_3 + Aq.$) is precipitated; but if dilute hydrochloric acid be carefully added to a 5 per cent. solution of tungstate of soda in sufficient proportion to neutralise the alkali, and the solution be then dialysed (p. 104), the chloride of sodium passes through, and a pure aqueous solution of tungstic acid is left in the dialyser. This solution is unchanged by boiling, and when evaporated to dryness, it forms vitreous scales, like gelatine, which adhere very strongly to the dish. It redissolves in one-fourth of its weight of water, forming a solution of the very high specific gravity 3·2, which is, therefore, able to float glass. The solution has a bitter and astringent taste, and decomposes carbonate of soda with effervescence. It becomes green when exposed to air, from the deoxidising action of organic dust. When the hydrated tungstic acid is heated, it loses water, and becomes of a straw-yellow colour and insoluble in acids. There are at least two modifications of tungstic acid, which bear to each other a relation similar to that between stannic and metastannic acids.

The most characteristic property of tungstic acid is that of yielding a blue oxide (WO_2, WO_3) when placed in contact with hydrochloric acid and metallic zinc.

A very remarkable compound containing tungstic acid and soda is obtained when bitungstate of soda ($NaO.2WO_3.4HO$) is fused with tin. If the fused mass be treated with strong potash, to remove free tungstic acid, washed with water, and treated with hydrochloric acid, yellow lustrous cubical crystals are obtained, which are remarkable, among sodium compounds, for their resistance to the action of water, of alkalies, and of all acids except hydrofluoric. The composition of these crystals appears to be $NaO.WO_2.2WO_3$.

The *binoxide of tungsten* (WO_2) appears to be an indifferent oxide, and is obtained by reducing tungstic acid with hydrogen at a low red heat, when it forms a brown powder which is dissolved by boiling in solution of potash, hydrogen being evolved, and tungstate of potash formed.

Metallic tungsten is obtained by reducing tungstic acid with charcoal at a white heat, as an iron-grey infusible metal of sp. gr. 17·6, very hard, not affected by hydrochloric or diluted sulphuric acid, but converted into tungstic acid by the action of nitric acid. When tungsten is dissolved in about ten times its weight of fused steel, it forms an extremely hard alloy.

When tungsten is heated in chlorine, the *terchloride of tungsten* (WCl_3) sublimes in bronze coloured needles, which are decomposed by water. When gently heated in hydrogen, it is converted into the bichloride (WCl_2), but if its vapour be mixed with hydrogen and passed through a glass tube heated to redness, metallic tungsten is obtained in a form in which it is not dissolved even by aqua regia, though it may be converted into tungstate of potash by hypochlorite of potash mixed with potash in excess.

Bisulphide of tungsten (WS_2) is a black crystalline substance resembling plumbago, obtained by heating a mixture of bitungstate of potash with sulphur, and washing with hot water. Tersulphide of tungsten (WS_3) is a sulphur-acid, obtainable as a brown precipitate by dissolving tungstic acid in an alkaline sulphide, and precipitating by an acid.

294. MOLYBDENUM derives its name from *μολύβδαινα, lead*, on account of the resemblance of its chief ore, *molybdena*, to black lead. Molybdena is the *bisulphide of molybdenum* (MoS_2), and is found chiefly in Bohemia and Sweden; it may be recog-

remarkable similarity to plumbago, and by its giving a blue solution with strong sulphuric acid. It is chiefly employed for the preparation of ammonia, which is used in testing for phosphoric acid. For this bisulphide of molybdenum is roasted in air at a dull red heat, when acid is evolved, and *molybdic acid* (MoO_3) mixed with oxide of iron is left. is digested with strong ammonia, which dissolves the molybdic acid in *molybdate of ammonia*, obtainable in prismatic crystals on evaporation. ution of molybdate of ammonia is added to a phosphate dissolved in c acid, a yellow precipitate of *phosphomolybdate of ammonia* is produced, ius molybdic and phosphoric acids combined with ammonia, by the for- hich very minute quantities of phosphoric acid can be detected. If acid be added in small quantity to a strong solution of molybdate of he molybdic acid is precipitated, but it is dissolved by an excess of acid, and if the solution be dialysed, the molybdic acid is obtained in an aqueous solution which reddens blue litmus, has an astringent taste, soluble gum-like residue when evaporated. Molybdic acid fuses at a a yellow glass, and may be sublimed in a current of air in shining contact with diluted hydrochloric acid and metallic zinc, it is con- a blue compound of molybdic acid with binoxide of molybdenum O_3) which is soluble in water, but is precipitated on adding a saline *olybdate of lead* ($PbO . MoO_3$) is found as a yellow crystalline mineral. *of molybdenum* (MoO_2) is basic, and forms dark red-brown salts. *Prot- ybdenum* (MoO) is obtained by adding an alkali to the solution resulting longed action of zinc upon a hydrochloric solution of molybdic acid. It ide which absorbs oxygen from the air.

olybdenum is obtained by reducing molybdic acid with charcoal at a white white metal, fusible with difficulty, unacted upon by hydrochloric and huric acids, but converted into molybdic acid by boiling with nitric rather a light metal, its specific gravity being 8·62. When heated in ields *bichloride of molybdenum* ($MoCl_2$), which forms a red vapour, and crystals resembling iodine, soluble in water. A *protochloride* (MoCl) is The *tersulphide* (MoS_3) and *tetrasulphide* (MoS_4) of molybdenum are s.

n to the natural sources of molybdenum above mentioned, there may *molybdic ochre* (an impure molybdic acid), and the difficultly fusible d *bear*, from the copper works in Saxony, which contain a large amount um combined with iron, copper, cobalt, and nickel.

ADIUM (*Vanadis*, a Scandinavian deity) was originally obtained from dish iron ores, but its chief ore is the *vanadiate of lead*, which is found in exico, and Chile. Vanadic acid has also been found in some clays, and erous sandstone at Perm in Russia. By treating the vanadiate of lead cid, expelling the excess of acid by evaporation, and washing out the ad with water, impure *vanadic acid* (VO_2) is obtained, which may be dissolving in ammonia, crystallising the vanadiate of ammonia, and it by heat, when vanadic acid is left as a reddish-yellow fusible solid, llises on cooling, and dissolves sparingly in water, giving a yellow solu- ssolves in hydrochloric acid, and if the solution be treated with a redu- such as hydrosulphuric acid) it assumes a fine blue colour, from the pro- ichloride of vanadium (VCl_2). If a solution of vanadiate of ammonia th tincture of galls, it gives an intensely black fluid, which forms an k, for it is not bleached by acids, alkalies, or chlorine. By heating with potassium, *metallic vanadium* is obtained as a white metallic powder, attacked by sulphuric or hydrochloric acid, but dissolves in nitric acid, ue solution of nitrate of binoxide of vanadium.

ide of vanadium (VO) appears to be an indifferent oxide. *Terchloride of* Cl_3) is a volatile yellow fuming liquid.

of vanadium (VS_2) is obtained as a black precipitate by the action of an hide upon the bichloride of vanadium ; it appears to be a sulphur-acid, es in an excess of the alkaline sulphide, fuming a purple solution.

ium (formerly called *columbium*) has been obtained from a rare dark grey line mineral known as *columbite*, occurring in Massachusetts. This ains *niobic acid* (NbO_2) combined with the oxides of iron and manganese. *acid is extracted* by a laborious process, and forms a white powder

sparingly soluble in hydrochloric acid. Niobium itself has been obtained as a bl powder insoluble in nitric acid and in aqua regia, but dissolved by a mixtur nitric and hydrofluoric acids.

Tantalum, formerly believed to be identical with niobium, occurs in the t and *yttrotantalite* of Sweden, which contain *tantalic acid* (TaO_2)* resembling ni acid.

Niobium and tantalum have recently been found to the amount of 2 or 3 p cent. in the tin ore of Moutebras.

PLATINUM.

297. Platinum (*platina*, Spanish diminutive of silver) is always fo in the metallic state, distributed in flattened grains through allu deposits similar to those in which gold is found; indeed, these grains generally accompanied by grains of gold, and of a group of very r metals only found in platinum ores, viz., palladium, iridium, osmi rhodium, and ruthenium. Russia furnishes the largest supply of platin from the Ural Mountains, but smaller quantities are obtained from Br Peru, Borneo, Australia, and California.

The process for obtaining the platinum in a marketable form is rat a chemical than a metallurgic operation. The ore containing the gr of platinum and the associated metals is heated with a dilute mixtur hydrochloric and nitric acids, by which the platinum is converted i bichloride of platinum ($PtCl_2$) and dissolved, whilst the iridium a osmium are left in the residue. The solution is then mixed with some chl ride of ammonium, which combines with the bichloride of platinum to form a yellow insoluble salt (ammonio-chloride of platinum, $NH_3 . HCl . PtCl_2$). This precipitate is collected, washed, and heated to redness, when all th constituents, except the platinum, are expelled in the form of gas, that metal being left in the peculiar porous condition in which it is known as *spongy platinum*. To convert this into compact platinum is by no means an easy task, on account of the infusibility of the metal, for it remains solid at the very highest temperatures of our furnaces. The spongy platinum is finely powdered in a wooden mortar (as it would cohere into metallic spangles in one of a harder material) and rubbed to a paste with water; this paste is then rubbed through a sieve to render it perfectly smooth and uniform, and introduced into a cylinder of brass, in which it is subjected to pressure so as to squeeze out the water and cause the minute particles of platinum to cohere into a somewhat compact disk; this disk is then heated to whiteness and beaten into a compact metallic ingot by a heavy hammer; it is then ready for forging.

A more modern process for obtaining platinum from its ores is based upon the tendency of this metal to dissolve in melted lead. The platinum ore is fused in a small reverberatory furnace, with an equal weight of sulphide of lead and the same quantity of oxide of lead, when the sulphur and oxygen escape as sulphurous acid, and the reduced lead dissolves the platinum, leaving undissolved a very heavy alloy of osmium and iridium which sinks to the bottom. The upper part of the alloy of lead and platinum is then ladled out and cupelled (page 353), when the latter metal is left in a spongy condition, the lead being removed in the form of oxide. The platinum is then fused by the aid of the oxyhydrogen blowpipe in a furnace made of lime (fig. 259), whence it is poured into an

* TaO_5 according to more recent experiments.

ıld made of gas-carbon. The melted platinum absorbs oxygen ally like melted silver, and evolves it again on cooling (*see*). Platinum articles are now frequently made from the fused stead of from that which has been welded.

istance to the action of high temperatures and of most chemical nders platinum of the greatest service in chemical operations. e remembered that platinum stills yed, even on the large scale, for the tion of sulphuric acid. In the form , small crucibles, foil, and wire, l is indispensable to the analytical Unfortunately, it is softer than ıd therefore ill adapted for wear, heavy (sp. gr. 21·5) that even ssels must be made very thin in to be too heavy for a delicate bal- nce it expands less than any other en heated, wires of platinum may be o glass without danger of splitting it al expansion. Its malleability and are very considerable, so that it is easily rolled into thin foil and to fine wires; in ductility it is surpassed only by gold and silver, s been drawn, by an ingenious contrivance of Wollaston's, into only $\frac{1}{30000}$th of an inch in diameter, a mile of which (notwith- the high specific gravity of the metal) would only weigh a single This remarkable extension of the metal was effected by casting a of silver around a very thin platinum wire obtained by the ordinary f wire-drawing. When the cylinder of silver, with the platinum its centre, was itself drawn out into an extremely thin wire, of ıe platinum core would have become inconceivably thin, and when r casing was dissolved off by nitric acid, this minute filament of ı was left. Platinum is sometimes employed for the touch-holes g-pieces on account of its resistance to corrosion. A little iridium mes added to platinum in order to increase its elasticity.

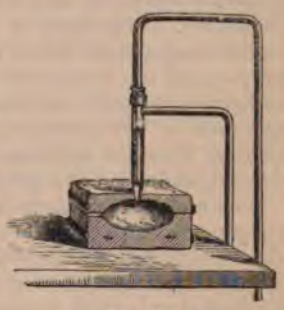


Fig. 259.

emarkable power possessed by platinum, of inducing chemical tion between oxygen and other gases, has already been noticed. e compact metal possesses this property, as may be seen by heat- ce of platinum foil to redness in the flame of a gauze gas-burner, extinguishing the gas, and turning it on again, when the cold f gas will still maintain the metal at a red heat, in consequence of ɔination with atmospheric oxygen at the surface of the platinum. ilar experiment may be made by suspending a coil of platinum he flame of a spirit-lamp (fig. 260), and suddenly out the flame when the metal is intensely heated; will continue to glow by inducing the combina- he spirit vapour with oxygen on its surface. By ing a little ball of spongy platinum for the coil um wire, and mixing some fragrant essential oil spirit, an elegant perfuming lamp has been con- Upon the same principle an instantaneous light is has been made, in which a jet of hydrogen gas ed by falling upon a fragment of cold spongy *, which at once ignites it* by inducing its combination with the

Fig. 260.

to light. Acids dissolve binoxide of platinum, forming salts colour which have not been crystallised. If binoxide of pla- ssolved in diluted sulphuric acid and the solution mixed with monia, a black precipitate of *fulminating platinum* is obtained, ates violently at about 400° F. This compound is said to osition corresponding to the formula NH_3, HO, PtO_2 + HO latinate of ammonia); and might also be represented as), or a combination of water with ammonia (NH_3), in which nts of hydrogen are replaced by one equivalent of platinum he binoxide, PtO_2, represents H_2).

of platinum.—The *bichloride*, or *platinic chloride* ($PtCl_2$), is eful salt of the metal, and may be prepared by dissolving tinum foil in a mixture of four measures of hydrochloric acid nitric acid (100 grains of platinum require 3 measured ounces oric acid), evaporating the liquid at a gentle heat to the con- a syrup, redissolving in dilute hydrochloric acid, and again to expel excess of nitric acid. The syrupy liquid solidifies o a red-brown mass, which is very deliquescent, and dissolves er or alcohol to a red-brown solution. If the concentrated llowed to cool before all the free hydrochloric acid has been g brown prismatic crystals of a combination of the bichloride hloric acid are obtained. The bichloride of platinum is re- its disposition to form sparingly soluble double chlorides with of the alkali metals and the hydrochlorates of organic bases, great value to the chemist in effecting the detection and sepa- se bodies.

xample of this has lately been afforded in the separation , rubidium, and cæsium. The chlorides of these three g been separated from the various other salts contained in water in which they occur, are precipitated with bichlo- um, which forms combinations with all the three chlorides. chloride of potassium is more easily dissolved by boiling hose of rubidium and cæsium, and is removed by boiling the pitate with small portions of water as long as the latter ellow colour. The remaining platino-chlorides of rubidium are then heated in a current of hydrogen, which reduces the the metallic state, and the chlorides may then be extracted which they are very soluble.

loride of potassium (KCl, $PtCl_2$) forms minute yellow octa- ls; those of rubidium and cæsium have a similar composition ne form.

loride of sodium differs from these in being very soluble in cohol; it may be crystallised in long red prisms, having the (NaCl, $PtCl_2$, 6Aq.)

chloride of platinum (NH_3. HCl, $PtCl_2$) has been already e form in which platinum is precipitated in order to separate metals. It crystallises, like the potassium-salt, in yellow hich are very sparingly soluble in water and insoluble in is the form into which nitrogen is finally converted in rder to determine its weight. When heated to redness, this residue of spongy platinum. The bichloride of platinum is ed for browning gun-barrels, &c., under the name of *muriate*

Protochloride of platinum or *platinous chloride* (PtCl).—The bichloride of platinum may be heated to 450° F. without decomposition, but above that temperature it evolves chlorine, and is slowly converted into the protochloride, which is reduced at a much higher temperature, to the metallic state. Platinous chloride forms a dingy green powder, which is insoluble in water and in nitric and sulphuric acids, but dissolves in hot hydrochloric acid, and in solution of platinic chloride, yielding in the former a bright red, in the latter a very dark brown-red solution. Its solution in hydrochloric acid is not precipitated by chloride of potassium, but a soluble double chloride (KCl, PtCl) may be crystallised from the liquid. If hydrochlorate of ammonia be added to the hydrochloric solution, a double salt of hydrochlorate of ammonia with protochloride of platinum ($NH_3 . HCl . PtCl$) may be obtained in yellow crystals by evaporation. If, instead of hydrochlorate of ammonia, free ammonia be added in excess to the boiling solution of protochloride of platinum in hydrochloric acid, brilliant green needles (green salt of Magnus) are deposited on cooling, which contain the elements of platinous chloride and ammonia ($PtCl . NH_3$), but from the behaviour of this compound with chemical agents, its true formula would appear to be $N_2H_5Pt . HCl$, PtCl, in which the place of 1 equivalent of hydrogen in two of ammonia is occupied by platinum. By heating this salt with an excess of ammonia, the platinous chloride which it contains may be decomposed, and when the solution is allowed to cool, it deposits yellowish-white prismatic crystals of *hydrochlorate of diplatosamine;* $N_2H_5Pt . HCl + Aq.$, the production of which may be represented by the equation—

$$N_2H_5Pt . HCl, PtCl + 2NH_3 = 2(N_2H_5Pt . HCl).$$

By decomposing a solution of this salt with sulphate of silver, the *sulphate of diplatosamine* is obtained; $N_2H_5Pt . HCl + AgO . SO_3 = N_2H_5Pt . HO . SO_3 + AgCl$.

When the solution of sulphate of diplatosamine is treated with hydrate of baryta, sulphate of baryta is precipitated, and a powerfully alkaline solution is obtained, which yields crystals of *hydrate of diplatosamine* $N_2H_5Pt . 2HO$, a strong alkali which may be regarded as a compound of water with 2 equivalents of ammonia (N_2H_6) in which 1 equivalent of hydrogen is replaced by platinum. The hydrate of diplatosamine has a strong resemblance to the hydrated mineral alkalies, eagerly absorbing carbonic acid from the air, and expelling ammonia from its salts. When the hydrate of diplatosamine is heated to 230° F. it gives off water and ammonia, and becomes converted into a grey insoluble substance, which is *hydrate of platosamine*, $NH_2Pt . HO$, and may be regarded as a compound of water with a single equivalent of ammonia (NH_3), in which one-third of the hydrogen is replaced by platinum. This substance is also a base, and forms salts, most of which are insoluble; the *sulphate of platosamine*, $NH_2Pt . HO . SO_3 + HO$, may be regarded as sulphate of ammonia ($NH_3 . HO . SO_3$), in which 1 equivalent of the hydrogen is replaced by platinum. The *hydrochlorate of platosamine* ($NH_2Pt . HCl$) is isomeric with the green salt of Magnus, and may be obtained from that compound by dissolving it in a hot solution of sulphate of ammonia, from which it crystallises on cooling.*

If the *hydrochlorate of platosamine*, suspended in boiling water, be treated with chlorine, it is converted into *hydrochlorate of platinamine*, $NHPt . 2HCl$, which may be represented as the hydrochlorate of an ammonia, in which 2 equivalents of hydrogen have been replaced by 1 equivalent of platinum in the condition in which it exists in the bichloride ($PtCl_2$), where it is equivalent to H_2. The conversion of the hydrochlorate of platosamine into hydrochlorate of platinamine may be represented by the equation, $NH_2Pt . HCl + Cl = NHPt . 2HCl$. By boiling the hydrochlorate of platinamine with nitrate of silver, it is converted into *nitrate of platinamine* ($NHPt . HO . NO_5$), and when this is dissolved in boiling water and decomposed by ammonia, the *hydrate of platinamine* ($NHPt, 4HO$) is obtained in yellow prismatic crystals, having the same composition as that assigned to fulminating platinum.

Several other platinum compounds derived from ammonia have been obtained, but cannot at present be so conveniently classified. The following table exhibits

* The salts of diplatosamine are distinguished from those of platosamine by the action of nitrous acid, which gives a fine blue or green precipitate or coloration with the former.

For the cause of this change, and for many other interesting points in the history of these platinum compounds, the author sorrowfully refers to the elaborate and accurate memoir by his lamented colleague, the late Mr Hadow, written during his last illness, and published in the Journal of the Chemical Society for August 1866, in which month he died, having there given a summary of the results of persevering and sagacious experimental work, extending over several years. He too truly wrote, that he was "prevented from making any further experiments for some time to come." He died August 11, 1866, aged

mposition of those here enumerated, the platinum, as it exists in platinous le ($PtCl$), occupying the place of 1 equivalent of hydrogen, being represented , and the platinum, as it exists in platinic chloride ($PtCl_2$), occupying the of 2 equivalents of hydrogen, by Pt″.

Hydrate of platosamine, . . .	$NH_2Pt'.HO$
Hydrochlorate of platosamine, . .	$NH_2Pt'.HCl$
Sulphate of platosamine, . . .	$NH_2Pt'.HO.SO_3 + HO$
Hydrate of platinamine, . . .	$NHPt''.4HO$
Hydrochlorate of platinamine, . .	$NHPt''.2HCl$
Hydrate of diplatosamine, . . .	$N_2H_5Pt'.2HO$
Hydrochlorate of diplatosamine, . .	$N_2H_5Pt'.HCl$
Sulphate of diplatosamine, . . .	$N_2H_5Pt'.HO.SO_3$

ne of the salts of *diplatinamine* (N_2H_4Pt'') have been obtained, this base being ed from two equivalents of ammonia in which H_2 have been replaced by Pt″. e *sulphides of platinum* correspond in composition to the oxides and chlorides, nay be obtained by the action of hydrosulphuric acid upon the respective chlo- as black precipitates.

9. *Equivalent and atomic weights of platinum.*—Platinic chloride, sed in its pure combination with chloride of potassium, is found to in 35·5 parts by weight (1 eq.) of chlorine combined with 49·3 parts tinum, and this latter number would represent the equivalent weight tinum if the platinic chloride contained a single equivalent of chlo- but since the platinous chloride contains only half as much chlorine e platinic chloride, it is usual to represent the former as containing and the latter 2 eqs. of chlorine combined with 1 eq. of platinum, at the equivalent weight of platinum (the quantity combined with rts or 2 eqs. of chlorine) would be 98·6, a view which is confirmed he composition of the ammonia derivatives containing platinum. pecific heat of platinum shows that its *atomic weight* must be twice its valent weight, or 197·2, and since, in the platinic compounds, which be regarded as the normal compounds of platinum, this weight of metal occupies the place of 4 atoms of hydrogen, platinum is gene- regarded as a tetratomic element ($Pt^{iv} = 197·2$), and the *atomic ulæ* of its chief compounds are written thus: platinous oxide, ; platinic oxide, PtO_2; platinous chloride, $PtCl_2$; platinic chloride, ; hydrate of platosamine, $N_2H_4Pt''.H_2O$; hydrate of platinamine, Pt^{iv}, $4H_2O$; hydrate of diplatosamine, $N_4H_{10}Pt''.2H_2O$.

). PALLADIUM is found in small quantity associated with native gold and pla- . It presents a great general resemblance to platinum, but is distinguished it by being far more easily oxidised, and by its special attraction for cyanogen, which it forms an insoluble compound. This circumstance is taken advantage separating palladium from the platinum ores, for which purpose the solution which the greater part of the platinum has been precipitated by hydrochlorate monia (p. 394) is neutralised with carbonate of soda, and mixed with solution anide of mercury (HgC_2N), when a yellowish precipitate of cyanide of pal- m is obtained, yielding spongy palladium when heated, which may be welded compact form in the same manner as platinum. When alloyed with native palladium is separated by fusing the alloy with silver, and boiling it with acid, which leaves the gold undissolved. The silver is precipitated from the ion as chloride by adding chloride of sodium, and metallic zinc is placed in the , which precipitates the palladium, lead, and copper, as a black powder. This solved in nitric acid, and the solution mixed with an excess of ammonia, which pitates the oxide of lead, leaving the copper and palladium in solution. On g hydrochloric acid in slight excess, a yellow precipitate of *hydrochlorate of pal- ine* ($NH_2Pd.HCl$) is obtained, which leaves metallic palladium when heated. *lladium is harder than platinum* and much lighter (sp. gr. 11·5); it is malle-

able and ductile like that metal, and somewhat more fusible, though it cannot be melted in an ordinary furnace.* It is unchangeable in air unless heated, when it becomes blue from superficial oxidation, but regains its whiteness when further heated, the oxide being decomposed. Unlike platinum, it may be dissolved by nitric acid, forming *nitrate of palladium* ($PdO . NO_5$), which is sometimes employed in analysis for precipitating iodine from the iodides, in the form of black *iodide of palladium* (PdI). Palladium is useful, on account of its hardness, lightness, and resistance to tarnish, in the construction of philosophical instruments; alloyed with twice its weight of silver, it is used for small weights.

Of the *oxides of palladium*, two correspond with those of platinum, and a basic *suboxide* (Pd_2O) has been obtained by gently heating the protoxide. *Bichloride of palladium* ($PdCl_2$) is very unstable, being easily decomposed, even in solution, into the *protochloride* (PdCl) and free chlorine. Both the chlorides form double salts with the alkaline chlorides, those containing the *palladious chloride* (PdCl) having a dark green colour. A pulverulent *carbide of palladium* is formed when the metal is heated in the flame of a spirit-lamp.

301. Rhodium, another of the metals associated with the ores of platinum, has acquired its name from the red colour of many of its salts (*ῥόδον, a rose*). It is obtained from the solution of the ore in *aqua regia* by precipitating the platinum with hydrochlorate of ammonia, neutralising with carbonate of soda, adding cyanide of mercury to separate the palladium, and evaporating the filtered solution to dryness with excess of hydrochloric acid. On treating the residue with alcohol, the double chloride of rhodium and sodium is left undissolved as a red powder. By heating this in a tube through which hydrogen is passed, the rhodium is reduced to the metallic state, and the chloride of sodium may be washed out with water, leaving a grey powder of metallic rhodium, which is fused by the oxyhydrogen blowpipe with greater difficulty than platinum, and forms a very hard malleable metal not dissolved even by *aqua regia*, although this acid dissolves it in the ores of platinum, because it is alloyed with other metals. If platinum be alloyed with 30 per cent. of rhodium, however, it is not affected by *aqua regia*, which will probably render the alloy useful for chemical vessels. Rhodium may be brought into solution by fusing it with bisulphate of potash, when sulphurous acid escapes, and a double sulphate of rhodium and potash is formed, which gives a pink solution with water. Finely divided rhodium is oxidised when heated in air. It appears to form two oxides, the *protoxide* (RoO), which is very little known, and the *sesquioxide* (Ro_2O_3), obtained by fusing rhodium with carbonate of potash and nitre, and washing the fused mass with water, which leaves an insoluble compound of the sesquioxide with potash; on treating this with hydrochloric acid, the sesquioxide of rhodium is left. It is not decomposed by heat, and is insoluble in acids, though it is a basic oxide, and its salts, which have a red colour, are obtained by indirect methods.

Sesquichloride of rhodium (Ro_2Cl_3) has a brownish black colour, and does not crystallise. Its aqueous solution is red, and it forms crystallisable double salts with the alkaline chlorides, which have a fine red colour. The double chloride of rhodium and sodium, $(3NaCl . Ro_2Cl_3) . 18Aq.$, is prepared by heating a mixture of pulverulent rhodium and chloride of sodium in a current of chlorine. It crystallises in red octahedra. On boiling a solution of sesquichloride of rhodium with ammonia in excess, a yellow ammoniated salt ($Ro_2Cl_3 . 5NH_3$) may be crystallised out, from which metallic rhodium may be obtained by ignition.

With sulphur, rhodium combines energetically at a high temperature; a protosulphide and a sesquisulphide have been obtained.

302. Osmium is characterised by its yielding a very volatile acid oxide (osmic acid, OsO_4), the vapours of which have a very irritating odour (*ὀσμή, odour*). It occurs in the ores of platinum in flat scales, consisting of an alloy of osmium, iridium, ruthenium, and rhodium. This alloy is also found associated with native gold, and being very heavy, it accumulates at the bottom of the crucible in which the gold is melted. The osmium alloy is extremely hard, and has been used to tip the points of gold pens. When a grain of it happens to be present in the gold which is being coined, it often seriously injures the die. When the platinum ore

* Palladium, at a slightly elevated temperature, absorbs, mechanically, many times its volume of hydrogen. Hammered palladium foil condenses 640 times its volume of hydrogen, below 212° F., though it has not the power of absorbing oxygen or nitrogen. Foil made from fused palladium only absorbs 68 times its volume of hydrogen.—(Graham, Proc. Roy. Soc., June 1866).

eated with *aqua regia*, this alloy is left undissolved, together with grains of me-iron ore and titanic iron. To extract the osmium from this residue, it is ed in a porcelain tube through which a current of dry air is passed, when the um is converted into osmic acid, the vapour of which is carried forward by the nt of air and condensed in bottles provided to receive it. The *osmic acid* forms rless prismatic crystals which fuse and volatilise below the boiling-point of r, yielding a most irritating vapour resembling chlorine. It is very soluble in r, giving a solution which exhales the odour of the acid and stains the skin ; tincture of galls gives a blue precipitate with the solution. Its acid pro- es are feeble, for it neither reddens litmus nor decomposes the carbonates, and lts are decomposed by boiling their solutions. By adding hydrosulphuric acid olution of osmic acid, the *tetrasulphide of osmium* (OsS_4) is obtained as a black pitate, and if this be carefully dried and heated in a crucible made of gas-carbon, *llic osmium* is obtained as a brittle mass (sp. gr. 21·4), which is not fused even e oxyhydrogen blowpipe, and is not soluble in acids. When obtained by other sses in a finely divided state, osmium oxidises even at the ordinary temperature, mits the odour of osmic acid. In this state, also, it may be dissolved by nitric which converts it into osmic acid.

y dissolving osmic acid in potash and adding alcohol, the latter is oxidised at expense of the osmic acid, and rose-coloured octahedral crystals of *osmite of sh* ($KO . OsO_3$, 2Aq.) are obtained ; the osmious acid has not been isolated. A oxide and a binoxide of osmium have been obtained.

smium appears to form four chlorides—*protochloride* (OsCl), *sesquichloride* Cl_3), *bichloride* ($OsCl_2$), and *terchloride* ($OsCl_3$). The protochloride and bichloride formed by the direct combination of chlorine with osmium ; the former sublimes reen needles, which yield a blue solution in water, soon absorbing oxygen from air and becoming converted into bichloride. By heating a mixture of pulverulent ium with chloride of potassium in a current of chlorine, a double chloride of ium and potassium ($KCl, OsCl_2$), is obtained which is sparingly soluble, and tallises in octahedra like the corresponding salt of platinum. When decom- d with nitrate of silver, it gives a dark green precipitate ($AgCl, OsCl_2$).

3. Ruthenium.*—In the process for extracting osmium from the residue left reating the platinum ore with *aqua regia*, by heating in a current of air, square natic crystals of *binoxide of ruthenium* (RuO_2) are deposited, nearer to the heated ion of the tube than the osmic acid, for the binoxide is not itself volatile, being carried forward mechanically in company with the osmic acid. When binoxide thenium is heated in hydrogen, *metallic ruthenium* is obtained as a hard, brittle, st infusible metal, which is scarcely affected even by *aqua regia*. The *pro- e of ruthenium* (RuO) is a dark grey powder insoluble in acids. The *sesquioxide* O_3) and the *binoxide* (RuO_2) have feebly basic properties. The sesquioxide t decomposed by heat. The anhydrous binoxide is a greenish blue powder. *enic acid* (RuO_3) is known only in combination with bases.

4. Iridium, named from *Iris, the rainbow*, in allusion to the varied colours of its ounds, has been mentioned above as occurring in the insoluble alloy from the num ores. It is also sometimes found separately, and occasionally alloyed with num, the alloy crystallising in octahedra, which are even heavier than platinum gr. 22·3). If the insoluble osmiridium alloy left by *aqua regia* be mixed with non salt and heated in a current of chlorine, a mixture of the sodio-chlorides of netals is obtained, and may be extracted by boiling water. If the solution be orated and distilled with nitric acid, the osmium is distilled off as osmic acid, by adding chloride of ammonium to the residual solution, the iridium is pre- ated as a dark red-brown ammonio-chloride (NH_3, HCl, $IrCl_2$) which leaves llic iridium when heated. Like platinum, it then forms a grey spongy mass, is oxidised when heated in air, and may be fused with the oxyhydrogen pipe to a hard brittle mass (sp. gr. 21·2), which does not oxidise in air. Like ium it is not attacked by *aqua regia*, unless alloyed with platinum. The pro- of the oxidation of finely divided iridium in air is the *sesquioxide* (Ir_2O_3), which black powder used for imparting an intense black to porcelain ; it is insoluble ids. The *protoxide* (IrO) is also more easily acted upon by alkalies than by ; its solution in potash becomes blue when exposed to air, from the formation

* A new mineral found in Borneo, and named *laurite*, contains sulphides of ruthenium smium. *It forms small lustrous granules.*

of the *binoxide* (IrO_2). The *teroxide* (IrO_3) is green. The *protochloride* (IrCl) a *bichloride* ($IrCl_2$) of iridium resemble the corresponding chlorides of platinum forming double salts with the alkaline chlorides. There is also a *sesquichlor* (Ir_2Cl_3), the solution of which has a green colour, and gives a yellow precipita with mercurous nitrate, and a blue precipitate, soon becoming white, with nitra of silver. Iridium resembles palladium in its disposition to combine with carb when heated in the flame of a spirit-lamp.

305. The following table exibits a general view of the analytical process by wh the remarkable metals associated in the ores of platinum may be separated fr each other, omitting the minor details which are requisite to ensure the purity each metal.

Analysis of the Ore of Platinum.

Boil with *aqua regia*.

<table>
<tr><td colspan="3">Dissolved.
Platinum, Palladium, Rhodium.
Add chloride of ammonium.</td><td colspan="3">Undissolved.
Iridium, Osmium, Ruthenium.
Chrome iron, Titanic iron, &c.
Heat in current of dry air.</td></tr>
<tr><td rowspan="2">Precipitated; Platinum as $NH_4Cl, PtCl_2$</td><td colspan="2">Solution; Neutralise with carbonate of soda; add cyanide of mercury.</td><td rowspan="2">Volatilised Osmium as OsO_4.</td><td rowspan="2">Carried forward by the current; Ruthenium as RuO_2.</td><td rowspan="2">Residue; Mix with chloride of sodium, and heat in current of chlorine. Treat with boiling wate</td></tr>
<tr><td>Precipitated; Palladium as PdCy.</td><td>Solution; Evaporate with hydrochloric acid. Treat with alcohol. Insoluble. Rhodium as $3NaCl.Ro_2Cl_3$.</td><td>Dissolved Iridium as $NaCl.IrCl_2$</td><td>Residue Titanic iro Chrome ir &c.</td></tr>
</table>

The group of *platinoid metals* exhibits some very remarkable features, and it i be regretted that it is comparatively imperfectly known in consequence of the d culty and expense attendant upon the purification of the metals. Its members s be arranged in two divisions, the metals in each agreeing closely in their equiva weights and specific gravities.

	Eq.	Sp. gr.		Eq.	S
Platinum, .	98·56	21·5	Palladium, .	53·24	
Osmium, . .	99·41	21·4	Rhodium, .	52·16	
Iridium, . .	98·56	21·2	Ruthenium, .	52·11	

Through osmium, this group of elements is connected with the group contai antimony, arsenic, and phosphorus, which osmium resembles in the facility which it is oxidised, and in the volatility of the oxide formed. Palladium com it with mercury and silver by its solubility in nitric acid, and its special attra for cyanogen and iodine.

GOLD.

306. Gold is one of those few metals which are always found in metallic state, and is remarkable for the extent to which it is distribu though in small quantities, over the surface of the earth. The prin supplies of this metal are derived from Australia, California, Me Brazil, Peru, and the Uralian Mountains. Small quantities have occasionally met with in our own islands, particularly at Wicklow Cader Idris in Wales, Leadhills in Scotland, and in Cornwall.

The mode of the occurrence of gold in the mineral kingdom resem that of the ore of tin, for it is either found disseminated in the prim rocks, or in alluvial deposits of sand, which appear to have been for by the disintegration of those rocks under the continued action of torr In the former case, the gold is often found crystallised in cubes and hedra, or in forms derived from these, and sometimes aggregated tog

dendritic or branch-like forms. In the alluvial deposits, the gold is ally found in small scales (gold dust), but sometimes in masses of con-erable size (nuggets), the rounded appearance of which indicates that y have been subjected to attrition.

The extraction of the particles of gold from the alluvial sands is effected taking advantage of the high specific gravity of the metal (19·3), which es it to remain behind, whilst the sand, which is very much lighter gr. 2·6), is carried away by water. This washing is commonly formed by hand, in wooden or metal bowls, in which the sand is ken up with water, and the lighter portions dexterously poured off, so o leave the grains of gold at the bottom of the vessel. On a somewhat er scale, the auriferous sand is washed in a cradle or inclined wooden gh, furnished with rockers, and with an opening at the lower end for the pe of the water. The sand is thrown on to a grating at the head of the le, which retains the large pebbles, whilst the sand and gold pass ugh, the former being washed away by a stream of water which is kept ing through the trough.

When the gold is disseminated through masses of quartz or other rock, h labour is expended in crushing the latter before the gold can be rated. This is effected either by passing the coarse fragments between y rollers of hard cast-iron, or by stamping them, with wooden beams d with iron, in troughs through which water is kept continually ing.

n some cases it is found advantageous to smelt the ore by fusing it h some substance capable of uniting with the gold, and of being after-ds readily separated from it. Lead is peculiarly adapted for this pur-e; the crushed ore, being mixed with a suitable proportion, either of allic lead, or of litharge (oxide of lead) and charcoal, or even of galena lphide of lead), together with some lime and oxide of iron or clay, to the silica, is fused on the hearth of a reverberatory furnace, when the d lead dissolves the particles of gold, and collects beneath the lighter . The lead is afterwards separated from the gold by cupellation (*see* 53).

n smelting the ores of gold in Hungary, the metal is concentrated by ns of sulphide of iron. The ore consists of quartz and iron pyrites ulphide of iron) containing a little gold. On fusing the crushed ore h lime, to flux the quartz, the pyrites loses half its sulphur, and becomes hide of iron (FeS), which fuses and sinks below the slag, carrying with he whole of the gold. If this product be roasted so as to convert the into oxide, and be then again fused with a fresh portion of the ore, oxide of iron will flux the quartz, whilst the fresh portion of sul-de of iron will carry down the whole of the gold contained in both ntities of ore. This operation having been repeated until the sulphide on is rich in gold, it is fused with a certain quantity of lead, which acts the gold and falls to the bottom. The lead is then cupelled in r to obtain the gold.

When the ores of lead, silver, or copper contain gold, it is always found ave accompanied the silver extracted from them, and is separated from a process to be presently noticed.

old is sometimes separated from the impurities remaining with it after action by washing, by the process of amalgamation, which consists in ing the mixture with mercury in order to dissolve the gold-dust, and *ning the liquid amalgam through* a chamois leather, which allows the

excess of mercury to pass through, but retains the solid portion contai the gold, from which the mercury is then separated by distillation.*

In the Tyrol, this process is adopted for separating the gold fro auriferous iron pyrites by grinding it in a mill of peculiar construct with water and a little mercury, the latter being allowed to act upon cessive portions of ore until it becomes sufficiently rich to be strained distilled.

Gold, as found in nature, is generally alloyed with variable propor of silver and copper, the separation of which is the object of the refiner. It may be effected by means of nitric acid, which will dis the silver and copper, provided that they do not bear too small a pro tion to the gold. Sulphuric acid, however, being very much cheap generally employed. The alloy is fused and poured into water, so a granulate it and expose a larger surface to the action of the acid; then boiled with concentrated sulphuric acid (oil of vitriol), which solves the silver and the copper in the form of sulphates, with evolu of sulphurous acid gas, whilst the gold is left untouched. In orde recover the silver from the solution, scraps of copper are introduced it, when that metal decomposes the sulphate of silver, producing sulp of copper, and causing the deposition of the silver in the metallic s Finally, the sulphate of copper may be obtained from the solution evaporation and crystallisation. This process is so effectual when proportion of gold in an alloy is very small, that even $\frac{1}{2000}$th part of metal may be profitably extracted from 100 parts of an alloy, and n gold has been obtained in this way from old silver-plate, coins, &c., w were manufactured before so perfect a process for the separation of t metals was known. On boiling old silver coins or ornaments with n acid, they are generally found to yield a minute proportion of gold in form of a purple powder. But this plan of separation is not so succe when the alloy contains a very large quantity of gold, for the latter n seems to protect the copper and silver from the solvent action of the Thus, if the alloy contains more than $\frac{1}{8}$th of its weight of gold, customary to fuse it with a quantity of silver, so as to reduce the pr tion of gold below that point, before boiling it with the acid. Aga the alloy contains a large quantity of copper, it is found expedie remove a great deal of this metal in the form of oxide by heating the in a current of air.

Pure gold, like pure silver, is too soft to resist the wear to which subjected in its ordinary uses, and it is therefore alloyed for coins this country with $\frac{1}{11}$th of its weight of copper, so that gold coin co 1 part of copper and 11 parts of gold. The gold used for artic jewellery is alloyed with variable proportions of copper and silver. alloy of copper and gold is much redder than pure gold.

The degree of purity of gold is generally expressed by quoting it so many carats fine. Thus, pure gold is said to be 24 carats fine; E standard gold is 22 carats fine, that is, contains 22 carats of gold the 24. Gold of 18 carats fine would contain 18 parts of gold out 24, or $\frac{3}{4}$ths of its weight of gold.

Pure gold is easily prepared from standard or jeweller's gold, by dissolvi hydrochloric acid mixed with one-fourth of its volume of nitric acid, eva the solution to a small bulk to expel excess of acid, diluting with a cons

* A small quantity of sodium dissolved in the mercury has been found very u to facilitate the amalgamation of gold and silver ores.

ty of water, filtering from the separated chloride of silver, and adding a solu- sulphate of iron, when the gold is precipitated as a dark purple powder, may be collected on a filter, well washed, dried, and fused in a small crucible little borax, the crucible having been previously glazed with borax to prevent on of the globules of gold. The action of the sulphate of iron upon the ter- le of gold is explained by the equation—

$$AuCl_3 + 6(FeO.SO_3) = Au + Fe_2Cl_3 + 2(Fe_2O_3.3SO_3).$$

employing oxalic acid instead of sulphate of iron, and heating the solution, ld is precipitated in a spongy state, and becomes a coherent lustrous mass pressure. The metal is employed in this form by dentists.

en standard gold is being dissolved in *aqua regia*, it sometimes becomes coated film of chloride of silver which stops the action of the acid; the liquid must e poured off, the metal washed, and treated with ammonia, which dissolves loride of silver; the ammonia must be washed away before the metal is re- in the acid. In the case of jeweller's gold, it is advisable to extract as much and copper as possible by boiling it with nitric acid, before attempting to dis- the gold. Gold lace should be incinerated to get rid of the cotton before being d with acid.

e genuineness of gold trinkets, &c., is generally tested by touching them with acid, which attacks them if they contain a very considerable proportion of r, producing a green stain, but this test is evidently useless if the surface be The weight is, of course, a good criterion in practised hands, but even these been deceived by bars of platinum covered with gold. The specific gravity e taken in doubtful cases; that of sovereign gold is 17·157.

assaying gold, the metal is wrapped in a piece of thin paper together with about times its weight of pure silver, and added to twelve times its weight of pure used in a bone-ash *cupel* (*see* page 355) placed in a muffle (or exposed to a oxidising blowpipe flame), when the lead and copper are oxidised, and the oxide of lead dissolves that of copper, both being absorbed by the cupel. the metallic button no longer diminishes in size, it is allowed to cool, ham- into a flat disk, which is annealed by being heated to redness, and rolled out in plate, so that it may be rolled up by the thumb and finger into a *cornet*, is boiled with nitric acid (sp. gr. 1·18) to extract the silver; the remaining s washed with distilled water, and boiled with nitric acid of sp. gr. 1·28 to t the last traces of silver, after which it is again washed, heated to redness in ll crucible, and weighed.

stronger nitric acid could not be used at first, since it would be likely to the cornet into fragments which could not be so readily washed without loss. ddition of the three parts of silver (*quartation*) is made in order to divide the and permit the easy extraction of the silver by nitric acid, which cannot be d when the gold predominates.

7. The physical characters of gold render it very conspicuous among the s; it is the heaviest of the metals in common use, with the exception tinum, its specific gravity being 19·3. In malleability and ductility passes all other metals; the former property is turned to advantage e manufacture of gold leaf, for which purpose a bar of gold is passed en rollers which extend it into the form of a riband; this is cut up squares, which are packed between layers of fine vellum, and beaten a heavy hammer; these thinner squares are then again cut up and n between layers of gold-beater's skin until they are sufficiently thin. unce of gold may thus be spread over 100 square feet; 282,000 of leaves placed upon each other form a pile of only one inch high. leaves will allow light to pass through them, and always appear or blue when held up to the light, though they exhibit the ordinary r of gold by reflected light; extremely thin leaves of gold, obtained artially dissolving ordinary gold leaf by floating it on solution of de of potassium, transmit a violet or a red light, according to their ness, though they still appear yellow by reflected light, and if taken *a glass plate and heated* to about 600° F. they lose their

golden reflection and become ruby red, changing to green if pressed with a hard substance. If very finely divided gold be suspended in water, it imparts a violet or red colour to it. Such coloured fluids containing very minute particles of gold in a state of suspension, may be obtained by the action of phosphorus dissolved in ether upon a very weak solution of gold in aqua regia; on standing for a long time, the particles of finely divided gold are deposited, having the same tint as that which they previously exhibited when suspended in the liquid; the blue particles being less minute are soonest deposited, but the red particles require many months to settle down. These divers colours of finely divided gold are taken advantage of in painting upon porcelain, and the well-known magnificent ruby red glass owes its colour to the same cause. $\frac{1}{11}$th of a grain of gold is capable of imparting a deep rose colour to a cubic inch of fluid.

The extreme ductility of gold is exemplified in the manufacture of gold thread for embroidery, in which a cylinder of silver having been covered with gold leaf, it is drawn through a wire-drawing plate and reduced to the thinness of a hair; in this way six ounces of gold are drawn into a cylinder two hundred miles in length. Although fusing at about the same temperature as copper, gold is seldom cast, on account of its great contraction during solidification.

Gold is not even affected to the same extent as silver by exposure to the atmosphere, for sulphuretted hydrogen has no action upon it, and hence no metal is so well adapted for coating surfaces which are required to preserve their lustre.

The gold is sometimes applied to the surfaces of metals in the form of an amalgam, the mercury being afterwards driven off by heat. Metals may also be gilt by means of a boiling solution prepared by dissolving gold in aqua regia, and adding an excess of bicarbonate of potash or of soda. But the most elegant process of gilding is that of electro-gilding, in which the object to be gilt is connected with the negative (zinc) end of the galvanic battery, and immersed in a solution of cyanide of gold in cyanide of potassium, in which is also placed a gold plate connected with the positive (copper) end of the battery, and intended, by gradually dissolving, to replace the gold abstracted from the solution at the negative pole.

A gold crucible is very useful in the laboratory for effecting the fusion of substances with caustic alkalies, which would corrode a platinum crucible.

308. *Oxides of gold.*—Two compounds of gold with oxygen have been obtained, AuO and AuO_3, but neither of them is of any great practical importance.

Teroxide of gold or *auric acid* (AuO_3) is prepared from the solution of gold in *aqua regia*, by boiling it with excess of potash, decomposing the aurate of potash with sulphuric acid, and purifying the auric acid by dissolving it in nitric acid and precipitating by water. It forms a yellow precipitate, which is easily decomposed by exposure to light or to a temperature of 500° F. By dissolving it in potash and evaporating *in vacuo* the *aurate of potash* is obtained in yellow needles ($KO.AuO_3$, 6A
Protoxide of gold (AuO) forms a dark precipitate when protochloride of gold is decomposed by potash.

The *chlorides of gold* correspond in composition to the oxides. The *terchloride of gold* ($AuCl_3$) is obtained by dissolving gold in hydrochlo

h one-fourth of its volume of nitric acid, and evaporating on a
ıth to a small bulk; on cooling, yellow prismatic crystals of a
nd of the terchloride with hydrochloric acid are deposited, from
he hydrochloric acid may be expelled by a gentle heat (not
ng ;250° F.), when the terchloride forms a red brown deliquescent
issolving very readily in water, giving a bright yellow solution
tains the skin and other organic matter purple when exposed to
epositing finely divided gold. Almost every substance capable of
ng with oxygen reduces the gold to the metallic state. The inside
fectly clean flask or tube may be covered with a film of metallic
a dilute solution of the terchloride mixed with citric acid and
a, and gently heated. The facility with which it deposits metallic
ıd the resistance of the deposited metal to atmospheric action, has
l terchloride of gold very useful in photography. Alcohol and
adily dissolve the terchloride, the latter being able to extract it
aqueous solution. Terchloride of gold (like bichloride of platinum)
rystallisable compounds with the alkaline chlorides and with the
ılorates of organic bases, and affords great help to the chemist in
these last. *Aurochloride of sodium* forms reddish yellow pris-
rystals ($NaCl . AuCl_3 . 4Aq.$) which are sometimes sold for photo-
purposes.

chloride of gold (AuCl) is obtained by gently heating the terchlo-
ıen it fuses and is decomposed at 350° F., leaving the protochloride,
s reduced to metallic gold at about 400° F. The protochloride is
ly soluble in water and of a pale-yellow colour. Boiling water
oses it into metallic gold and terchloride.

inating gold is obtained as a buff precipitate when ammonia is
solution of terchloride of gold; its composition is not well estab-
but appears to be $AuO_3 . 2NH_3 . HO$. It explodes violently when
ıeated.

Sel d'or of the photographer is a hyposulphite of gold and soda
S_2O_2, $3(NaO . S_2O_2)$, 4Aq.), which is obtained in fine white needles
ing a solution of one part of terchloride of gold into a solution of
arts of hyposulphite of soda, and adding alcohol, in which the
alt is insoluble. Its formation may be explained by the equation—

$$8(NaO . S_2O_2) + AuCl_3 =$$
$$AuO . S_2O_2, 3(NaO . S_2O_2) + 3NaCl + 2(NaO . S_4O_5).$$

ubtful whether the above formula represents the true constitution
salt, for it is not decomposed by acids in the same manner as ordi-
posulphites. Nitric acid causes the whole of the gold to separate
netallic state.

le of Cassius, which is employed for imparting a rich red colour to
d porcelain, is a compound of gold, tin, and oxygen, which are be-
be grouped according to the formula $AuO . SnO_2 . SnO . SnO_2 + 4Aq.$
be prepared by adding protochloride of tin to a mixture of bi-
of tin and terchloride of gold; 7 parts of gold are dissolved in
gia and mixed with 2 parts of tin also dissolved in *aqua regia*;
ution is largely diluted with water, and a weak solution of 1 part
ı hydrochloric acid is added, drop by drop, till a fine purple colour
ıced. The purple of Cassius remains suspended in water in a very
te of division, but subsides gradually, especially if some saline
be added, as a purple powder. The fresh precipitate dissolves in

ammonia, but the purple solution is decomposed by exposure to light, becoming blue, and finally colourless, metallic gold being precipitated, and binoxide of tin left in solution.

The *sulphides of gold* are not thoroughly known. When hydrosulphuric acid acts on solution of terchloride of gold, a black precipitate of AuS, AuS_3 is obtained, which dissolves in alkaline sulphides. The salt NaS, AuS, 8Aq. has been obtained, in colourless prisms soluble in alcohol. The precipitated sulphide of gold is not dissolved by the acids, with the exception of *aqua regia*. Nitric acid oxidises the sulphur, leaving metallic gold. When hydrosulphuric acid is added to a boiling solution of terchloride of gold, the metal itself is precipitated—

$$4AuCl_3 + 3HS + 12HO = Au_4 + 12HCl + 3(HO.SO_3).$$

309. *Equivalent and atomic weights of gold.*—Terchloride of gold, analysed in its crystalline compound with chloride of potassium, was found to contain 35·5 parts by weight (1 eq.) of chlorine in combination with 65·53 parts of gold. The existence of a chloride containing three times as much gold in combination with the above weight of chlorine leads to the belief that the equivalent of gold should be represented by 65·53 × 3, or 196·6. The specific heat of gold shows that its *atomic weight* is also 196·6, so that the atomic formulæ of its chief compounds are—protoxide, Au_2O; auric acid, Au_2O_3; aurous chloride, AuCl; auric chloride, $AuCl_3$. Gold is usually considered a triatomic element, occupying the place of three atoms of hydrogen.

ON SOME OF THE

SEFUL APPLICATIONS OF CHEMICAL PRINCIPLES NOT HITHERTO MENTIONED.

CHEMICAL PRINCIPLES OF THE MANUFACTURE OF GLASS.

310. Glass is defined chemically to be a mixture of two or more silicates, e of which is a silicate of an alkali, the other being a silicate of lime, ryta, oxide of iron, oxide of lead, or oxide of zinc.

If silicic acid be fused with an equal weight of carbonate of potash or da, a transparent glassy mass is obtained, but this is slowly dissolved by ter, and would therefore be incapable of resisting the action of the ather; if a small proportion of lime or baryta, or of the oxides of iron, d, or zinc, be added, the glass becomes far less easily affected by atmo-heric influences.

The most valuable property of glass, after its transparency and per-nence, is that of assuming a viscid or plastic consistency when fused, ich allows it to be so easily fashioned into the various shapes required use or ornament.

The composition of glass is varied according to the particular purpose which it is intended, the materials selected being fused in large clay ucibles placed in reverberatory furnaces, and heated by a coal-fire or in gas-furnace.

Ordinary *window glass* is essentially composed of silicate of soda and icate of lime, containing one equivalent (13·3 per cent.) of soda, one uivalent (12·9 per cent.) of lime, and five equivalents (69·1 per cent.) of icic acid; it also usually contains a little alumina. This variety of glass manufactured by fusing 100 parts of sand with about 35 parts of chalk d 35 parts of soda-ash: a considerable quantity of broken window glass always fused up at the same time. Of course, the carbonic acid of the alk and of the carbonate of soda is expelled in the gaseous state, and in der that this may not cause the contents of the crucible to froth over ring the fusion, the materials are first *fritted* together, as it is termed, a temperature insufficient to liquefy them, when the carbonic acid evolved gradually, and the fusion afterwards takes place without ervescence.

Occasionally sulphate of soda is employed instead of the carbonate, en it is usual to add a small proportion of charcoal, in order to reduce *sulphuric to the state of* sulphurous acid, which is far more easily

expelled. Before the glass is worked into sheets, it is allowed to remain at rest for some time in the fused state, so that the air-bubbles may escape, and the *glass-gall* or scum (consisting chiefly of sulphate of soda and chloride of sodium), which rises to the surface, is removed.

Plate glass is also chiefly a silicate of soda and lime, but it contains, in addition, a considerable quantity of silicate of potash (74 per cent. of silicic acid, 12 of soda, 5·5 of potash, and 5·5 of lime). The purest white sand is selected, and great care is taken to exclude impurities.

Crown glass, used for optical purposes, contains no soda, since this alkali has the property of imparting a greenish tint to glass, which is not the case with potash. This variety of glass, therefore, is prepared by fusing sand with carbonate of potash and chalk in such proportions that the glass may contain one equivalent (22 per cent.) of potash, one equivalent (12·5 per cent.) of lime, and four equivalents (62 per cent.) of silicic acid.

The glass of which *wine bottles* are made is of a much cheaper and commoner description, consisting chiefly of silicate of lime, but containing, in addition, small quantities of the silicates of the alkalies, of alumina, and of oxide of iron, to the last of which it owes its dark colour. It is made of the coarsest materials, such as common red sand (containing iron and alumina), soap-makers' waste (containing lime and small quantities of alkali), refuse lime from the gas-works, clay, and a very small proportion of rock-salt.

Flint glass, which is used for table glass and for ornamental purposes, is a double silicate of potash and oxide of lead, containing one equivalent (13·67 per cent.) of potash, one equivalent (33·28 per cent.) of oxide of lead, and six equivalents (51·93 per cent.) of silicic acid. It is prepared by fusing 300 parts of the purest white sand with 200 parts of minium (red oxide of lead), 100 parts of refined pearl-ash, and 30 parts of nitre. The fusion is effected in crucibles covered in at the top to prevent the access of the flame, which would reduce a portion of the lead to the metallic state. The nitre is added in order to oxidise any accidental impurities which might reduce the lead.

The presence of the oxide of lead in glass very much increases its fusibility, and renders it much softer, so that it may be more easily cut into ornamental forms; it also greatly increases its lustre and beauty.

Baryta has also the effect of increasing the fusibilty of glass, and oxide of zinc, like oxide of lead, increases its brilliancy and refracting power, on which account it is employed in some kinds of glass for optical purposes. Glass of this description is also made by substituting boracic acid for a portion of the silicic acid.

Some varieties of glass, if heated nearly to their melting point, and allowed to cool slowly, become converted into an opaque very hard mass resembling porcelain (*Réaumur's porcelain*). This change, which is known as *devitrification*, is due to the crystallisation of the silicates contained in the mass, and by again fusing it the glass may be restored to its original transparent condition.

In producing *coloured glass*, advantage is taken of its property of dissolving many metallic oxides with production of peculiar colours. It has been mentioned above that bottle glass owes its green colour to the presence of oxide of iron; and since this oxide is generally found in small quantity in sand, and even in chalk, it occasionally happens that a glass which is required to be perfectly colourless turns out to have a slight green tinge. In order to remove this, a small quantity of some oxidising agent

is usually added, in order to convert the oxide of iron into the sesquioxide, which does not impart any colour when present in minute proportion. A little nitre is sometimes added for this purpose, or some arsenious acid, which yields its oxygen to the oxide of iron, and escapes in the form of vapour of arsenic; red oxide of lead (Pb_3O_4) may also be employed, and is reduced to oxide of lead (PbO), which remains in the glass. Binoxide of manganese is often added as an oxidising agent, being reduced to the state of oxide of manganese (MnO), which does not colour the glass; but care is then taken not to add too much of the binoxide, for a very minute quantity of this substance imparts a beautiful amethyst purple colour to glass.

Suboxide of copper is used to produce a red glass, and the finest ruby glass is obtained (as already mentioned at p. 406) by the addition of a little gold. The oxides of antimony impart a yellow colour to glass; a peculiar brown-yellow shade is given by charcoal in a fine state of division, and sesquioxide of uranium produces a fine greenish-yellow glass. Green glass is coloured either by oxide of copper or sesquioxide of chromium, whilst oxide of cobalt gives a magnificent blue colour. For black glass, a mixture of the oxides of cobalt and manganese is employed. The white enamel glass is a flint glass, containing about 10 per cent. of binoxide of tin. Bone ash is also used to impart this appearance to glass.

CHEMISTRY OF THE MANUFACTURE OF POTTERY AND PORCELAIN.

311. The manufacture of pottery obviously belongs to an earlier period of civilisation than that of glass, since the raw material, clay, would at once suggest, by its plastic properties, the possibility of working it into useful vessels, and the application of heat would naturally be had recourse to in order to dry and harden it. Indeed, at the first glance, it would appear that this manufacture, unlike that of glass, did not involve the application of chemical principles, but consisted simply in fashioning the clay by mere mechanical dexterity into the required form. It is found, however, at the outset, that the name of *clay* is applied to a large class of minerals, differing very considerably in composition, and possessing in common the two characteristic features of plasticity and a predominance of silicate of alumina.

It has already been stated (p. 286) that *kaolin* is a hydrated silicate of alumina, and it is from this material that the best variety of porcelain is made. This clay is eminently plastic, and can therefore be readily moulded, but when baked, it shrinks very much, so that the vessels made from it lose their shape and often crack in the kiln. In order to prevent this, the clay is mixed with a certain proportion of sand, chalk, bone-ash, or heavy-spar; but another difficulty is thus introduced, for these substances diminish the tenacity of the clay, and would thus render the vessels brittle. A further addition must therefore be made, of some substance which fuses at the temperature employed in baking the ware, and thus serves as a cement to bind the unfused particles of clay, &c., into a compact mass. Feldspar (silicate of alumina and potash) answers this purpose; or carbonate of potash or of soda is sometimes added, to convert a portion of the silica into a fusible alkaline silicate. With a mixture of clay with sand and feldspar (or some substitutes), a vessel may be moulded *which will preserve its shape* and tenacity when baked, but it will be

easily pervious to water, and thus quite unfit for ordinary use. It has, therefore, to be water-proofed by the application of some easily fusible material, which shall either form a glaze over the surface, or shall become incorporated with the body of the ware, and the vessel is then fit for all its uses. Handles and ornaments in relief are moulded separately, and fixed on the ware before baking, and coloured designs are transferred from paper to the porous ware before glazing.

The manufacture of *Sèvres porcelain* is one of the most perfect examples of this art. The purest materials are selected in the following proportions :—Kaolin (porcelain clay), 62 parts ; chalk, 4 parts ; sand, 17 parts; feldspar, 17 parts. These materials are ground up with water before being mixed, and the coarser particles allowed to subside ; the creamy fluids containing the finer particles in suspension are then mixed in the proper proportions, and allowed to settle ; the paste deposited at the bottom is drained, thoroughly kneaded, and stored away for some months in a damp place, by which its texture is considerably improved, and any organic matter which it contains becomes oxidised and removed; the oxidation being effected partly by the sulphates present, which become reduced to sulphides. It is then moulded into the required forms, and dried by simple exposure to the air. The vessels are packed in cylindrical cases of very refractory clay, which are arranged in a furnace or kiln of peculiar construction, and very gradually but strongly heated by the flame of a wood fire. When sufficiently baked, the *biscuit* porcelain has to be glazed, and great care is taken that the glaze may possess the same expansibility by heat as the ware itself, for otherwise it would crack in all directions as the glazed ware cooled. The glaze employed at Sèvres is a mixture of feldspar and quartz very finely ground, and suspended in water, to which a little vinegar is added to prevent the glaze from subsiding too rapidly. When the porous ware is dipped into this mixture, it absorbs the water, and retains a thin coating of the mixture of quartz and feldspar upon its surface. It is now baked a second time, when the glaze fuses, partly penetrating the ware, partly remaining as a varnish upon the surface.

When the ware is required to have some uniform colour, a mineral pigment capable of resisting very high temperatures is mixed with the glaze ; but coloured designs are painted upon the ware after glazing, the ware being then baked a third time, in order to fix the colours. These colours are glasses coloured with metallic oxides, and ground up with oil of turpentine, so that they may be painted in the ordinary way upon the surface of the ware ; when the latter is again heated in the kiln, the coloured glass fuses, and thus contracts a firm adhesion with the ware.

Gold is applied either in the form of precipitated metallic gold, or of fulminating gold, being ground up in either case with oil of turpentine, burnt in, and burnished.

English porcelain is made from Cornish clay mixed with ground flints, burnt bones, and sometimes a little carbonate of soda, borax, and binoxide of tin, the last improving the colour of the ware. It is glazed with a mixture of Cornish stone (consisting of quartz and feldspar), flint, chalk, borax, and sometimes white lead to increase its fusibility.

Stone-ware is made from less pure materials, and is covered with a glaze of silicate of soda, in a very simple manner, by a process known as *salt-glazing*. The ware is coated with a thin film of sand by dipping it in a mixture of fine sand and water, and is then intensely heated in a kiln into

which a quantity of damp salt is presently thrown. The joint action of the aqueous vapour and the salt converts the sand into silicate of soda, which fuses into a glass upon the surface of the ware—

$$NaCl + HO + SiO_2 = NaO . SiO_2 + HCl .$$

Pipkins, and similar earthenware vessels are made of common clay mixed with a certain proportion of marl and of sand. They are glazed with a mixture of 4 or 5 parts of clay, with 6 or 7 parts of litharge. The colour of this ware is due to the presence of peroxide of iron.

Bricks and tiles are also made from common clay mixed, if necessary, with sand. These are very often grey, or blue, or yellow, before baking, and become red under the action of heat, since the iron, which is originally present as carbonate ($FeO . CO_2$), becomes converted into the red peroxide (Fe_2O_3) by the atmospheric oxygen.

The impure varieties of clay fuse much more easily than pure clay, so that, for the manufacture of the refractory bricks for lining furnaces, of glass-pots, crucibles for making cast steel, &c., a pure clay is employed, to which a certain quantity of broken pots of the same material is added, to prevent the articles from shrinking whilst being dried.

Dinas fire-bricks are made from a peculiar siliceous material found in the Vale of Neath, and containing alumina with about 98 per cent. of silica. The ground rock is mixed with 1 per cent. of lime and a little water before moulding. These bricks are expanded by heat, whilst ordinary fire-bricks contract.

Blue bricks are glazed by sprinkling with *iron scurf*, a mixture of particles of stone and iron produced by the wear of the siliceous grindstones employed in grinding gun-barrels, &c. When the bricks are fired, a glaze of silicate of iron is formed upon them.

CHEMISTRY OF BUILDING MATERIALS.

312. Chemical principles would lead to the selection of pure silica (quartz, rock-crystal) as the most durable of building materials, since it is not acted on by any of the substances likely to be present in the atmosphere; but even if it could be obtained in sufficiently large masses for the purpose, its great hardness presents an obstacle to its being hewn into the required forms. Of the building stones actually employed *granite*, *basalt*, and *porphyry* are the most lasting, on account of their capability of resisting for a great length of time the action of water and of atmospheric carbonic acid; but their hardness makes them so difficult to work, as to prevent their employment except for the construction of pavements, bridges, &c., where the work is massive and straightforward, and much resistance to wear and tear is required. The *millstone grit* is also a very durable stone, consisting chiefly of silica, and employed for the foundations of houses. *Freestone* is a term applied to any stone which is soft enough to be wrought with hammer and chisel, or cut with a saw; it includes the different varieties of sandstone and limestone. The sandstones consist of grains of sand cemented together by clay or limestone. The *Yorkshire flags* employed for paving are siliceous stones of this description. The *Craigleith sandstone*, which is one of the freestones used in London, contains about 98 per cent. of silica, together with some carbonate of lime.

The building stones in most general use are the different varieties of carbonate of lime. The durability of these is in proportion to their *compact structure; thus marble*, being the most compact, has been found to

resist for many centuries the action of the atmosphere, whilst the more porous limestones are corroded at the surface in a very short time. *Portland stone*, of which St Paul's and Somerset House are built, and *Bath stone*, are among the most durable of these; but they are all slowly corroded by exposure to the atmosphere. The chief cause of this corrosion appears to be the mechanical disintegration caused by the expansion, in freezing, of the water absorbed in the pores of the stone. In order to determine the relative extent to which different stones are liable to be disintegrated by frost, a test has been devised, which consists in soaking the stone repeatedly in a saturated solution of sulphate of soda and allowing it to dry, when the crystallisation of the salt disintegrates the stone, as freezing water would, so that if the particles detached from the surface be collected and weighed, a numerical expression for the resistance of the material will be obtained. *Magnesian limestones* (carbonate of lime with carbonate of magnesia) are much valued for ornamental architecture, on account of the ease with which they may be carved, and are said to be more durable in proportion as they approach the composition expressed by the formula $CaO . CO_2$, $MgO . CO_2$.* The magnesian limestone from Bolsover Moor, of which the Houses of Parliament are built, contains 50 per cent. of carbonate of lime, 40 of carbonate of magnesia, with some silica and alumina.

It is probable that a slow corrosion of the surface of limestone is effected by the carbonic acid continually deposited in aqueous solution from the air; and it is certain that in the atmosphere of towns the limestone is attacked by the sulphuric acid which results from the combustion of coal and the operations of chemical works. The Houses of Parliament have suffered severely, probably from this cause. Many processes have been recommended for the preservation of building stones, such as waterproofing them by the application of oily and resinous substances, and coating or impregnating them with solution of soluble glass and similar matters; but none seems yet to have been thoroughly tested by practical experience.

Purbeck, *Ancaster*, and *Caen stones* are well-known limestones employed for building.

313. The *mortar* employed for building is composed of 1 part of freshly slaked lime and 2 or 3 parts of sand intimately mixed with enough water to form an uniform paste. The hardening of such a composition appears to be due, in the first instance, to the absorption of carbonic acid from the air, by which a portion of the lime is converted into carbonate, and this, uniting with the unaltered hydrate of lime, forms a solid layer adhering closely to the two surfaces of brick or stone, which it cements together. In the course of time, the lime would act upon the silica, producing silicate of lime, and this chemical action would render the adhesion more perfect. The chief use of the sand here, as in the manufacture of pottery (p. 411), is to prevent excessive shrinking during the drying of the mortar.

In constructions which are exposed to the action of water, mortars of peculiar composition are employed. These *hydraulic mortars* or *cements*, as they are termed, are prepared by calcining mixtures of carbonate of lime with from 10 to 30 per cent. of clay, when the carbonic acid is expelled, and the lime combines with a portion of the silicic acid from the

* Any excess of carbonate of lime above that required by this formula may be dissolved out by treating the powdered magnesian limestone with weak acetic acid.

, producing a silicate of lime, and probably also, with the alumina, to aluminate of lime. When the calcined mass is ground to powder mixed with water, the silicates of alumina and lime, and the aluminate me, unite to form hydrated double silicates and aluminates, upon which r has no action. Roman cement is prepared by calcining a limestone aining about 20 per cent. of clay, and hardens in a very short time mixing with water.

r Portland cement (so called from its resembling Portland stone) cture of river-mud (chiefly clay) and limestone is calcined at a very temperature.

ncrete is a mixture of hydraulic cement with small gravel. A speci- of this material from a very ancient Phœnician temple was as hard rock, and contained nearly 30 per cent. of pebbles.

ott's cement is prepared by passing air containing a small quantity of urous acid, evolved from burning sulphur, over quick-lime heated to redness. The setting of this cement appears due to the presence of all proportion of sulphate of lime very intimately mixed with the k-lime.

GUNPOWDER.

14. Gunpowder is a very intimate mixture of saltpetre (nitre or te of potash), sulphur, and charcoal, which do not act upon each r at the ordinary temperature, but when heated together arrange nselves into new forms, evolving a very large amount of gas.

n order to manufacture gunpowder capable of producing the greatest ible effect, great attention is requisite to the purity of the ingredients, process of mixing, and the form ultimately given to the finished der.

HEMISTRY OF THE INGREDIENTS OF GUNPOWDER—SALTPETRE.—*Nitrate otash* ($KO.NO_5$), *nitre* or *saltpetre*, is found in some parts of India, cially in Bengal and Oude, where it sometimes appears as a white in- ation on the surface of the soil, and is sometimes mixed with it to depth. The nitre is extracted from the earth by treating it with r, and the solution is evaporated, at first by the heat of the sun, and wards by artificial heat, when the impure crystals are obtained, which packed in bags and sent to this country as *grough* (or impure) salt-. It contains a quantity of extraneous matter varying from 1 to 10 ent., and consisting of the chlorides of potassium and sodium, sul- es of potash, soda, and lime, vegetable matter from the soil, sand, and ture. The number representing the weight of impurity present is lly termed the *refraction* of the nitre, in allusion to the old method timating it by casting the melted nitre into a cake and examining its ure, the appearance of which varies according to the amount of gn matter present.

ruvian or *Chili saltpetre* is the *nitrate of soda* ($NaO.NO_5$) found in and Chili in beds beneath the surface soil. It is often spoken of as *al saltpetre*, since it crystallises in rhombohedra, easily mistaken for s, whilst *prismatic saltpetre*, nitrate of potash, crystallises in six-sided as. Nitrate of soda cannot be substituted for nitrate of potash as an dient of gunpowder, since it attracts moisture from the air, becoming , and appears to be less powerful in its oxidising action upon com- *ble bodies at a high temperature*. The Peruvian saltpetre, however,

forms a very important source from which to prepare the nitrate of potash for gunpowder, since it is easily converted into this salt by double decomposition with chloride of potassium. The latter salt is now imported in so large a quantity from the salt mines of Stassfurth (p. 261), that it enables nitrate of soda to be very cheaply converted into nitrate of potash, and renders Indian saltpetre of less importance to the manufacturer of gunpowder.

In order to understand the production of saltpetre by the decomposition of nitrate of soda with chloride of potassium, it is necessary to be acquainted with the solubility of those salts and of the salts produced by their mutual decomposition.

100 parts of boiling water dissolve			100 parts of cold water dissolve		
218	parts	of nitrate of soda,	50	parts	of nitrate of soda,
53	,,	chloride of potassium,	33	,,	chloride of potassium,
200	,,	nitrate of potash,	30	,,	nitrate of potash,
37	,,	chloride of sodium.	36	,,	chloride of sodium.

It is a general rule that when two salts in solution are mixed, which are capable of forming, by exchange of their metals, a salt which is less soluble in the liquid, that salt will be produced and separated.

Thus when nitrate of soda and chloride of potassium are mixed, and the solution boiled down, chloride of sodium is deposited, and nitrate of potash remains in the boiling liquid—

$$NaO.NO_5 + KCl = KO.NO_5 + NaCl.$$

When this is allowed to cool, the greater part of the nitrate of potash crystallises out, leaving the remainder of the chloride of sodium in solution.

The method usually adopted is to add the chloride of potassium by degrees to the boiling solution of nitrate of soda, to remove the chloride of sodium with a perforated ladle in proportion as it is deposited, and, after allowing the liquid to rest for some time to deposit suspended impurities, to run it out into the crystallising pans.

The potash-salt required for the conversion of nitrate of soda into nitrate of potash is sometimes obtained from the refuse of the beet root employed in the manufacture of sugar.

Nitrate of potash is sometimes prepared from the nitrates obtained in the *nitre-heaps*, which consist of accumulations of vegetable and animal refuse with limestone, old mortar, ashes, &c. These heaps are constructed upon an impermeable clay floor under a shed to protect them from rain. One side of the heap is usually vertical and exposed to the prevailing wind, the other side being cut into steps or terraces. They are occasionally moistened with stable drainings, which are allowed to run into grooves cut in the steps at the back of the heap. In such a mass, at an atmospheric temperature between 60° and 70° F., nitrates of the various bases present in the heap are slowly formed, and being dissolved by the moisture, are left by it, as it evaporates on the vertical side, in the form of an efflorescence. When this has accumulated in sufficient quantity, it is scraped off, together with a few inches of the *nitrified* earth, and extracted with water, which dissolves the nitrates, whilst the undissolved earth is built up again on the terraced back of the heap. After two or three years the heap is entirely broken up and reconstructed. The principal nitrates which are found dissolved in the water are those of potash,

nesia, and ammonia, the three last of which may be converted te of potash by decomposing them with carbonate of potash.
rmation of nitric acid in these heaps probably results from che-nges similar to those which occur in the soils in which nitre lly formed, but, at present, these changes are not thoroughly . Some chemists are of opinion that the nitric acid is formed nion of atmospheric nitrogen and oxygen, encouraged by the of porous solids, and of matters undergoing oxidation. The on which is best supported by experimental evidence is that ers the formation of nitric acid to the oxidation of ammonia evolved by the putrefaction of the nitrogenised matters which s contain, this oxidation also being much promoted by the of the strongly alkaline lime, and of the porous materials capable ng ammonia and presenting it under circumstances favourable on.

ing saltpetre for the manufacture of gunpowder, the impure salt ed in about an equal weight of boiling water in a copper boiler, ion run through cloth filters to remove insoluble matter, and o crystallise in a shallow wooden trough lined with copper, the f which is formed of two inclined planes (fig. 261). Whilst he solution is kept in continual agitation with wooden stirrers, that the saltpetre may be deposited in the ystals known as *saltpetre flour*, and not in prisms which are formed when the solution d to crystallise tranquilly, and which con-in them cavities enclosing some of the quor from which the saltpetre has been d. The saltpetre, being so much less cold than in hot water, is, in great part, as the liquid cools, whilst the chlorides impurities being present in small propor-not presenting the same disparity in their at different temperatures, are retained in d. The saltpetre flour is drained in a rough with a perforated bottom, and trans-a washing-cistern, where it is allowed to r half an hour in contact with two or three successive small of water to wash away the adhering impure liquor; it is then o drain thoroughly, and in that state, containing from three to nt. of water, according to the season, is ready to be transferred corporating mill or to a hot-air oven, where it is dried if not for immediate use.

Fig. 261.

other-liquor, from which the saltpetre flour has been deposited, down and crystallised, the crystals being worked up with the h of grough nitre. The final washings of the flour are returned iler in which the grough nitre is originally dissolved. When tre contains very much colouring matter, a little glue or animal s employed by the refiner to assist in its removal.

l method of refining saltpetre consisted in crystallising it three arge crystals, which were afterwards melted into cakes or *cheeses*. frequently happened that the fusion was effected at too high a ire, when a portion of the nitrate of potash became converted te *of potash* ($KO.NO_5$). The test for *overfused nitre* was solu-

tion of sulphate of copper, which gave a green colour, due to the production of nitrite of copper.

The impurities most objectionable in the saltpetre employed for gunpowder would be the chlorides of potassium and sodium, which cause it to absorb moisture easily from the air; the chief test, therefore, to which the refiner subjects it, is the addition, to its solution in distilled water, of a few drops of solution of nitrate of silver, which causes a milkiness, due to the separation of a precipitate of chloride of silver, if the chlorides have not been entirely removed. Moreover, the sample should dissolve entirely in water, to a perfectly clear colourless solution, which should have no effect on blue or red litmus paper, and should give no cloudiness with chloride of barium (indicating the presence of sulphates), or with oxalate of ammonia (indicating lime), when these are added to separate portions of it. Very minute quantities of sulphates and of lime, such as may have been derived from the use of river water in washing the flour, are generally disregarded.

315. *Properties of saltpetre.*—Nitrate of potash is usually distinguishable by the long striated or grooved six-sided prismatic form in which it crystallises (though it may also be obtained in rhombohedral crystals like those of nitrate of soda), and by the *deflagration* which it produces when thrown on red-hot coals. It fuses at about 660° F. to a colourless liquid, which solidifies on cooling to a translucent brittle crystalline mass. The *sal prunelle* of the shops consists of nitre which has been fused and cast into balls. At a red heat it effervesces from the escape of bubbles of oxygen, and is converted into nitrite of potash ($KO.NO_3$), which is itself decomposed by a higher temperature, evolving nitrogen and oxygen, and leaving a mixture of potash and peroxide of potassium. In contact with any combustible body, it undergoes decomposition with great rapidity, the five equivalents of oxygen in the nitric acid (NO_5) being available for the oxidation of the combustible substance, and the nitrogen being evolved in the free state; thus, in contact with carbon, the decomposition of the nitre may be represented by the equation—

$$2(KO.NO_5) + C_5 = 2(KO.CO_2) + 3CO_2 + N_2.$$

Since the combustion of a large quantity of material may be thus effected in a very small space and in a short time, the temperature produced is much higher than that obtained by burning the combustible in the ordinary way. The specific gravity of saltpetre is 2·07, so that one cubic inch weighs 523 grains (obtained by multiplying the weight of a cubic inch of water, 252·5 grains by 2·07). Since 101 grains (1 eq.) of nitre contain 40 grains (5 eqs.) of oxygen available for the oxidation of combustible bodies, 523 grains, or one cubic inch, of nitre, would contain 200 grains or 605 cubic inches of available oxygen, a volume which would be contained in about 3000 cubic inches of air; hence, one volume of saltpetre represents, in its power of supporting combustion, 3000 volumes of atmospheric air. It also enables some combustible substances to burn without actual flame, as is exemplified by its use in *touch-paper* or *slow port-fire*, which consists of paper soaked in a weak solution of saltpetre and dried.

If a continuous design be traced on foolscap paper with a brush dipped in a solution of 30 grains of saltpetre in 100 grains of water, and allowed to dry, it will be found that when one part of the pattern is touched with a red-hot iron, it will gradually burn its way out, the other portion of the paper remaining unaffected.

of 90 grains of saltpetre, 30 of sulphur, and 30 of moderately fine saw-
's flux), will deflagrate with sufficient intensity to fuse a small silver
globule: the mixture may be pressed down in a walnut shell or a small
ucible, and the coin buried in it, the flame of a lamp being applied out-
flagration commences.
minans is a mixture of 3 parts of saltpetre, 1 part of sulphur, and 2 of
potash, all carefully dried; when it is heated on an iron plate, no action
till it begins to melt, when it explodes very violently.

ARCOAL FOR GUNPOWDER.—Charcoal has been already described
lue of the destructive distillation of wood, in which process the
nd oxygen of the wood are for the most part expelled in the
wood naphtha ($C_2H_4O_2$), pyroligneous acid ($C_4H_4O_4$), carbonic
nic oxide, water, &c., leaving a residue containing a much
ortion of carbon than the original wood, and therefore capable
ng a much higher temperature (p. 61) by its combustion with
re. The higher the temperature to which the charcoal is
its preparation, the larger the proportion of hydrogen and
elled, and the more nearly does the charcoal approach in com-
pure carbon; but it is not found advantageous in practice to
high a temperature, since it yields a dense charcoal of difficult
lity, and therefore less fitted for the manufacture of powder.
owing table exhibits the composition of dried alder-wood and
rcoal obtained at different temperatures. The incombustible
sh of the wood and charcoal is here omitted.

arts.	Temperature of charring.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.
od, . .	...	48·63	5·94	44·75	0·68
. . .	518° F.	71·0	4·6	24·4	
	662°	77·2	4·1	18·7	
	800°	82·6	1·9	15·5	
	2000°	83·3	2·3	14·4	
	2300°	89·2	1·4	9·4	
	2700°	95·4	0·7	3·9	
	Above 3000°	98·8	0·6	0·6	

e shows that at temperatures between 800° and 2000° F., there
e alteration in the composition of the charcoal, and it is within
s that the charcoal employed for the manufacture of gunpowder
ntry is prepared. Between these limits, however, the density
uent inflammability of the charcoal vary considerably, that
t the lower temperatures igniting most readily. Hence it is
hat the temperature of carbonisation should not exceed an
w red heat (about 1000° F.)
rcoal prepared between 500° and 600° F. has a brown colour
oux), and although it is more easily inflamed than the black
tained at higher temperatures, the presence of so large a pro-
oxygen so much diminishes its calorific value, that its employ-
npowder is not advantageous. It is used on the Continent in
acture of sporting-powder, and is prepared by exposing the
n iron cylinder, to the action of high-pressure steam heated to
F. The *charbon roux* is very hygroscopic.
oods, such as alder, willow, and dogwood (cornel tree), are

selected for the preparation of charcoal for gunpowder, because they yield a lighter and more easily combustible charcoal, dogwood being employed for the best quality of powder. This wood is chiefly imported, since it has not been successfully grown in this country. The wood is stripped of its bark, and either exposed for a length of time to the air or dried in a hot chamber. Considerable loss of charcoal takes place if damp wood be charred, a portion of the carbon being oxidised by the steam at a high temperature.

In order to convert the wood into charcoal, 1½ cwt. of wood is packed into a sheet iron cylinder or *slip* (fig. 262), one end of which is closed by a tightly fitting cover, and the other by a perforated plate, to allow of the escape of the gases and vapours expelled during the carbonisation. This cylinder is then introduced into a cylindrical iron retort built into a brick furnace, and provided with a pipe (L) for the escape of the products, which are usually carried back into the furnace (B) to be consumed. The process of charring occupies from 3½ to 4 hours, and as soon as it is completed, the slip is transferred to an iron box or *extinguisher*, where the charcoal is allowed to cool. About 40 lbs. of charcoal are obtained from the above quantity of wood. Charcoal prepared by this process is spoken of as *cylinder charcoal*, to distinguish it from *pit charcoal*, prepared by the ordinary process of charcoal-burning described at (p. 57), and which is employed for fuze compositions, &c., but not for the best gunpowder. The fitness of the charcoal for the manufacture of powder is generally judged of by its physical characters. It is of course desirable that the charcoal should be as free from incombustible matter as possible. The proportion of the ash left by different charcoals varies considerably, but it seldom exceeds two per cent. This ash consists chiefly of the carbonates of potash and lime; it also contains phosphate of lime, carbonate of magnesia, silicate and sulphate of potash, chloride of sodium, and the oxides of iron and manganese.

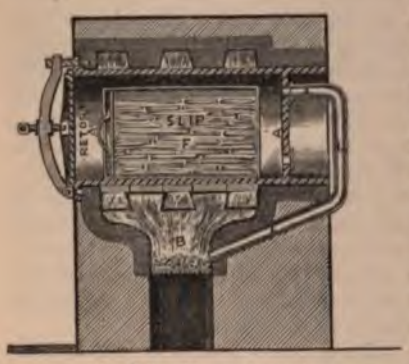


Fig. 262.—Charcoal retort.

The properties of charcoal have been already described; its great tendency to absorb moisture from the air is of some importance in the manufacture of gunpowder, from its causing a false estimate to be made of the proportion employed, unless the actual amount of water present in the charcoal is known.

Tar charcoal is the name given to sticks of charcoal which have accidentally become coated with a shining film of carbon left behind by tar which has condensed upon it in the retorts; it is sometimes rejected by the powder manufacturer.

317. SULPHUR FOR GUNPOWDER.—*Distilled sulphur* (p. 185) is the variety always employed for the manufacture of gunpowder, the *sublimed sulphur* being employed for fuze compositions, &c. The alleged reason for the preference is that the sublimed sulphur, having been deposited in a chamber containing much sulphurous and sulphuric acid

apours, its pores have become charged with acid which would be injurious n the powder; but it has been pointed out (p. 187) that distilled sul-hur consists entirely of the soluble or electro-negative variety of sulphur, whilst sublimed sulphur contains a large proportion of the insoluble or positive sulphur, which would probably influence its action in gunpowder. The sulphur should leave scarcely a trace of incombustible matter when burnt, and after stirring the powdered sulphur for some time with warm distilled water, the latter should only very feebly redden blue litmus. As an ingredient of gunpowder, sulphur is valuable on account of the low temperature (560° F.) at which it inflames, thus facilitating the ignition of the powder. Its oxidation by saltpetre appears also to be attended with the production of a higher temperature than is obtained with charcoal, which would have the effect of accelerating the combustion and of increasing, by expansion, the volume of gas evolved.

The difference in the inflammability of sulphur and charcoal is strikingly shown by heating a square of coarse wire gauze over a flame till it is red hot in the centre, placing it over a jar of oxygen, allowing it to cool till it no longer kindles charcoal-powder sprinkled through it from a pepper-box, and whilst the cloud of charcoal is still floating in the gas, throwing in sulphur from a second box; the hot gauze will inflame the sulphur, and this will kindle the charcoal.

An iron rod allowed to cool below redness may be used to stir a mixture of charcoal with (3 parts of) nitre; but if it be dipped into powdered sulphur, at once inflames it, and the flame of the sulphur will kindle the mixture. The effect of the same rod upon mixtures of nitre with charcoal alone, and with charcoal and sulphur, is instructive.

The acceleration of the combustion of gunpowder by the sulphur is well shown by laying a train, of which one-half consists of a mixture of 75 nitre and 25 charcoal, and the other of 75 nitre, 15 charcoal, and 10 sulphur, a red-hot iron being applied at the junction of the two trains to start them together.

318. MANUFACTURE OF GUNPOWDER.—The proportions of the ingredients of gunpowder have been varied somewhat in different countries, the saltpetre ranging from 74 to 77 per cent., the charcoal from 12 to 16, and the sulphur from 9 to 12·5 per cent. English Government powder contains—

75	per cent.	of nitre.
15	„	charcoal.
10	„	sulphur.

The powdered ingredients are first roughly mixed in a revolving copper drum, with mixing arms turning in an opposite direction, and the mixture is subjected, in quantities of about 50 lbs. at a time, to the action of the *incorporating mill* (fig. 263), where it is sprinkled with water, poured through the funnel (F), or from a can with a fine rose, and exposed to trituration and pressure under two cast-iron edge-runners (B), rolling round in different paths upon a cast-iron bed, a very intimate mixture being thus effected by the same kind of movement as in a common pestle and mortar, the distribution of the nitre through the mass being also *assisted by its solubility in* water. A wooden scraper (C) tipped with

Fig. 263.—Incorporating mill.

copper, prevents the roller from getting clogged, and a *plough* (D) keeps the mixture in the path. Of course, the water employed to moisten the powder must be as free from deliquescent salts (especially chlorides, *see* p. 418) as possible; the quantity required varies with the state of the atmosphere. The duration of the incorporating process is varied according to the kind of powder required, the slow-burning powder employed for cannon being sufficiently incorporated in about 3½ hours, whilst rifle-powder requires 5 hours.

The dark-grey slaty mass of *mill-cake*, which is thus produced, is broken up by passing between grooved rollers of gun metal, and is then placed, in layers of about an inch thick, between copper plates packed in a stout box, in which it is subjected for a quarter of an hour to a pressure of about 70 tons on the square foot, in a hydraulic press, which has the effect of condensing a larger quantity of explosive material into a given volume, and of diminishing the tendency of the powder to absorb moisture from the air and to disintegrate or *dust* after granulation. The *press-cake* thus obtained is very hard and compact, resembling slate in appearance. As far as its chemical nature is concerned, it is finished gunpowder, but if it be reduced to powder and a gun loaded with it, the combustion of the charge is found to take place too slowly to produce its full effect, since the pulverulent form offers so great an obstacle to the passage of the flame by which the combustion is communicated from one end of the charge to the other. The press-cake must, therefore, be *granulated* (*corned*) or broken up into grains of sufficient size to allow the rapid passage of the flame between them, and the consequent immediate firing of the whole charge. The granulation is effected by crushing the press cake between successive pairs of toothed gun metal rollers, from which it falls on to sieves, which separate it into grains of different sizes, the dust, or *meal powder*, passing through the last sieve. The granulated powders are freed from dust by passing them through revolving cylinders of wooden frame-work covered with canvas, and the fine grain powder is glazed by the friction of its own grains against each other in revolving barrels. The large grain powders are sometimes glazed or *faced* with graphite, by introducing a little of that substance into the glazing-barrels with the powder. The powder is dried in a hot-air chamber very gradually, so as not to injure the grain, and is once more dusted in canvas cylinders before being packed.

Various modifications are introduced into the above processes in different places, but the principles upon which the manufacture is conducted are always the same.

319. PROPERTIES OF GUNPOWDER.—Good gunpowder is composed of hard angular grains, which do not soil the fingers, and have a perfectly uniform dark-grey colour. Its specific gravity (*absolute density*) appears to vary between 1·84 and 1·97, and its *apparent density* (obtained by weighing a given measure of the grain against an equal measure of water) varies from 0·89 to 0·94, so that a cubic foot will weigh from 55 to 58 lbs. When exposed to air of average dryness, gunpowder absorbs about 0·5 per cent. of water. In damp air it absorbs a much larger proportion, and becomes deteriorated in consequence of the saltpetre being dissolved, and [illegible]allising upon the surface of the grains. Actual contact with water [illegible]s the saltpetre and disintegrates the grains. When very gradually [illegible]n air, gunpowder begins to lose sulphur, even at 212° F., this passing off rapidly as the temperature rises, so that the greater

part of it may be expelled without inflaming the powder, especially if the powder is heated in carbonic acid or hydrogen, to prevent contact with air. If gunpowder be suddenly heated to 600° F. in air, it explodes, the sulphur probably inflaming first; but out of contact with air a higher temperature is required to inflame it. The ignition of gunpowder by flame is not ensured unless the flame be flashed among the grains of powder; it often takes some time to ignite powder with the flame of a piece of burning paper or stick, but contact with a red-hot solid body inflames it at once. A heap of good powder, when fired on a sheet of white paper, burns without sparks and without scorching or kindling the paper, which should exhibit only scanty black marks of charcoal after the explosion. If the powder has not been thoroughly incorporated, it will leave minute globules of fused nitre upon the paper. Two ounces of the powder should be capable of throwing a 68-lb. shot to a distance of 260 to 300 feet from an 8-inch mortar at 45° elevation.

Very fortunately, it is difficult to explode gunpowder by concussion, though it has been found possible to do so, especially on iron, and accidents appear to have been caused in this way by the iron edge-runners in the incorporating mill, when the workmen have neglected the special precautions which are laid down for them. The use of stone upon iron in the incorporation is avoided, because of the great risk of producing sparks, and copper is employed in the various fittings of a powder mill wherever it is possible.

The electric spark is, of course, capable of firing gunpowder.

320. Products of explosion of gunpowder.—In the explosion of gunpowder, the oxygen of the nitre converts the carbon of the charcoal chiefly into carbonic acid (CO_2), part of which assumes the gaseous state, whilst the remainder combines with the potash of the nitre to form carbonate of potash ($KO.CO_2$). The greater part of the sulphur is converted into sulphuric acid (SO_3), which forms sulphate of potash ($KO.SO_3$). The chief part of the nitrogen contained in the nitre is evolved in the uncombined state. The rough chemical account of the explosion of gunpowder, therefore, is that the mixture of nitre, sulphur, and charcoal is resolved into a mixture of carbonate of potash, sulphate of potash, carbonic acid, and nitrogen, the two last being gases, the elastic force of which, when expanded by the heat of the combustion, accounts for the mechanical effect of the explosion.

But in addition to these, several other substances are found among the products of the explosion. Thus, the presence of sulphide of potassium (KS) may be recognised by the smell of hydrosulphuric acid produced on moistening the solid residue in the barrel of a gun, and hydrosulphuric acid (HS) itself may often be perceived in the gases produced by the explosion, the hydrogen being derived from the charcoal. A little marsh-gas (C_2H_4) is also found among the gases, being produced by the decomposition of the charcoal, a portion of the hydrogen of which is also disengaged in the free state. Carbonic oxide (CO) is always detected among the products. It is evident that the collection for analysis of the products of explosion must be attended with some trouble, and that considerable differences are to be expected between the results obtained by different operators, from the variation of the circumstances under which the powder is fired and the products collected. When the powder is *slowly burnt, a considerable proportion* of the nitrogen in the saltpetre is

evolved in the form of nitric oxide gas (NO_2), which is not found among the products of the rapid explosion of powder.

Some of the most recent experiments upon the explosion of gunpowder have been made under conditions very similar to those which occur in practice, the powder having been confined in a thin iron case and suspended in the centre of a strong iron globe exhausted of air, in which the powder was fired by electricity, so that the gaseous and solid products of the explosion remained within the globe, and could be submitted to analysis. Two samples of powder were thus examined, but their composition differed from that of English Government powder stated above, as will be seen by the following table:—

	I.		II.
Nitre,	73·78	...	77·15
Sulphur,	12·80	...	8·63
Charcoal, viz., Carbon,	10·88	...	11·78
Hydrogen,	0·38	...	0·42
Oxygen,	1·82	...	1·79
Ash,	0·31	...	0·28
	99·97		100·05

About 570 grs. of powder were exploded in each experiment. The gas collected was found to be inflammable, as would be expected from the flash which is always perceived at the muzzle when a gun is discharged.

100 grs. of sample I. gave 107·4 cub. in. of gas at 32° F. and 30 in. Bar.
" " II. " 117·5 " " "

The gases contained, in 100 cubic inches—

	I.		II.
Nitrogen,	37·58	...	35·33
Carbonic acid (CO_2),	42·74	...	48·90
Carbonic oxide (CO),	10·19	...	5·18
Hydrogen,	5·93	...	6·90
Sulphuretted hydrogen (HS),	0·86	...	0·67
Marsh-gas (C_2H_4),	2·70	...	3·02
	100·00		100·00

The products of explosion furnished by 100 grains of each powder, were—

	I.		II.
Sulphate of potash ($KO.SO_3$),	36·95	...	36·17
Carbonate of potash ($KO.CO_2$),	19·40	...	20·78
Hyposulphite of potash ($KO.S_2O_2$),	2·85	...	1·77
Sulphide of potassium (KS),	0·11	...	0·00
Sesquicarbonate of ammonia,	2·68	...	2·66
Charcoal,	2·57	...	2·60
Sulphur,	4·69	...	1·16
Nitrogen,	9·77	...	10·06
Carbonic acid (CO_2),	17·39	...	21·79
Carbonic oxide (CO),	2·64	...	1·47
Hydrogen,	0·11	...	0·14
Sulphuretted hydrogen (HS),	0·27	...	0·23
Marsh-gas (C_2H_4),	0·40	...	0·49
	99·88		99·82

both these cases it will be seen that if the charcoal and sulphur took no part in the combustion be left out of consideration, the

ate and carbonate of potash formed together more than $\frac{8}{9}$ of the products of explosion; and that the carbonic acid and nitrogen together amounted, in the one case to $\frac{9}{10}$, and in the other to $\frac{1}{17}$ of aseous products. If only the chief products of the explosion be into consideration, viz., sulphate and carbonate of potash, carbonic carbonic oxide, and nitrogen, the following equation is the simplest h can be constructed from the above numerical data :—

$$7(KO.NO_5) + S_4 + C_{12} = 4(KO.SO_3) + 3(KO.CO_2) + 8CO_2 + N_7 + CO.$$

is equation, however, would represent a gunpowder composed of

Nitre, . . .	83·8
Sulphur, . .	7·5
Charcoal, . .	8·5
	99·8

would require the products of decomposition to be—

Sulphate of potash, . .	41·2
Carbonate of potash, . .	24·5
Carbonic acid, . . .	20·8
Nitrogen, ...	11·6
Carbonic oxide, . . .	1·6
	99·7

asoning from analogy with other chemical operations, it seems pro- that the explosion of gunpowder really includes a number of ical changes which cannot be simply represented in one equation, hat whilst the above equation, or some similar one, represents the ipal reaction which takes place during the explosion, there are other r reactions in progress, the products of which are found in smaller ity.

1. Calculation of the force of fired gunpowder.—The mechani- orce exerted in the explosion of gunpowder depends upon the pro- on of a large volume of gas from a small volume of solid, the volume e gas being increased by the expansive effect of the heat generated e combustion of the charcoal and sulphur. To calculate the amount is mechanical force, it is necessary to ascertain the volume of gas would be evolved by a given volume of powder, and the extent to this gas would be expanded by the heat at the instant of explosion. order to illustrate this calculation, let it be assumed that the equa- given above correctly represents the explosion of the powder, viz.—

$$7(KO.NO_5) + S_4 + C_{12} = 4(KO.SO_3) + 3(KO.CO_2) + 8CO_2 + N_7 + CO.$$

w, it is known, as a result of experimental determination, that

7 eqs. nitrate of potash	(101 × 7)	=	707 grains.
4 eqs. sulphur	(16 × 4)	=	64 „
12 eqs. carbon	(6 × 12)	=	72 „
Gunpowder, . .			843 „

					At 60° F., and 30 in. Bar.
8 eqs. carbonic acid	(22 × 8)	=	176 grains	=	372·0 cub. inches.
7 eqs. nitrogen	(14 × 7)	=	98 „	=	325·4 „
1 eq. carbonic oxide		=	14 „	=	46·5 „
					743·9 „

Hence it appears that 843 grains of gunpowder would yield 743·9 cubic inches of gas measured at 60° F. and 30 in. barometric pressure.

If one cubic foot of the powder weighs 58 lbs., one cubic inch will weigh 234·9 grains, and will evolve 207 cubic inches of gas measured at 60° F. and 30 in. Bar.

But the mechanical force exerted by the powder depends upon the volume of this gas at the period of explosion, and in order to calculate this, we must ascertain what would be its temperature at that period.

A carefully conducted experiment has shown that the explosion of one part by weight of gunpowder is able to raise the temperature of 619·5 parts by weight of water from 0° C. to 1° C., or to raise the temperature of one part by weight of water from 0° C. to 619°·5 C., supposing the water to be capable of bearing so great an elevation of temperature without change of state.

This result is generally expressed by saying that the combustion of the powder evolves 619·5 *units of heat* (the unit of heat being the quantity required to raise 1 part by weight of water from 0° C. to 1° C.)

But the products of the explosion of powder will be raised to a higher temperature than 619°·5 C., because their specific heat is lower than that of water.

For the purpose of this calculation, the specific heat of a substance may be defined as the quantity of heat required to raise 1 gr. of the substance through 1° of the thermometer, water being taken as the unit.

It is evident that if the specific heat of each product of the explosion be multiplied by the actual weight of that product, the result will be the quantity of heat required to raise that product 1° in temperature.

The specific heats of the products have been ascertained by experiment, and are contained in the first column of figures in the following table. The actual weight of each product from the explosion of 1 gr. of powder is contained in the second column, and the third column shows the quantity of heat required to raise each product 1° C. (representing as unity the quantity of heat required to raise 1 gr. of water from 0° C. to 1° C.)

	Spec. Heat.		From 1 gr. powder.		
Sulphate of potash, .	0·1901	×	0·412	=	0·07832
Carbonate of potash,	0·2162	×	0·246	=	0·05319
Carbonic acid,	0·2164	×	0·209	=	0·04523
Nitrogen,	0·2440	×	0·116	=	0·02830
Carbonic oxide,	0·2479	×	0·017	=	0·00421
					0·20925

The quantity of heat, therefore, which is required to raise, through 1° C., the joint products of the explosion of one grain of gunpowder is 0·20925 of the above-mentioned unit.

Dividing the 619·5 units of heat generated in the explosion, by the ity of heat required to raise the joint products through one degree, 20925, we obtain 2960° C. (= 5328° F.) for the number

ees through which the products will be raised by the explosion, *i.e.*, he temperature of the products at the moment of explosion.*

remains to be ascertained what volume would be occupied, at 5328° by the 207 cubic inches of gas at 60° F. evolved from one cubic inch owder.

he expansion which gases suffer when heated amounts to $\frac{1}{491}$ of their ume at 32° F. for each degree Fahrenheit.

Thus 491 volumes of gas at 32° F. become
492 „ „ 33° F.,

if heated 28° above 32°, *i.e.*, to 60° F., they would become 491 + 28, 19 volumes. If the 491 volumes be heated to 5328° F., or 5296° ve 32°, they will expand to 491 + 5296, or 5787 volumes.

he volume of the gas at the moment of explosion, therefore, will be rtained from the following proportion—

Vols. at 60° F.		Vols. at 5328° F.		Cub. in. at 60° F.		Cub. in. at 5328° F.
519	:	5787	: :	207	:	2308

which it appears that one cubic inch of powder would evolve a tity of gas measuring 2308 cubic inches at the moment of ex- ion.

ince the pressure exerted by gases upon the sides of a containing e is inversely as their volume, the gas evolved from a cubic inch of der, if developed in a space exactly filled by the powder, would exert ressure of 2308 atmospheres, or 34,620 lbs., or 15½ tons upon the re inch.

t is here supposed, of course, that the whole of the gas is evolved at e, and is immediately raised to the same temperature, conditions never lled in the use of gunpowder in small arms or in cannon, where the bustion of the charge is not instantaneous but rapidly progressive, re the confining space is rapidly enlarged by the movement of the jectile long before the whole of the charge has exploded, and where heated gas is cooled by contact with the metal of the piece.

he period over which the combustion of a given weight of powder ex- ds will, of course, depend upon the extent of surface over which it be kindled; thus a single fragment of powder weighing 10 grains, n if it were instantaneously kindled over its entire surface, could not lve so much gas in a given time as if it had been broken into ten arate grains, each of which was kindled at the same instant, since the ide of the large fragment can only be kindled from the outside. Upon s principle a given weight of powder in large grains will occupy a ger period in its explosion than the same weight in small grains, so t the large grain powder is best fitted for ordnance, where the ball is y heavy, and the time occupied in moving it will permit the whole of charge to be fired before the ball has left the muzzle, whilst in small s with light projectiles, a finer grained and more quickly burning rge is required. If the fine grain powder were used in cannon, the ole of the gas might be evolved before the containing space had been sibly enlarged by the movement of the heavy projectile, and the gun ld be subjected to an unnecessary strain; on the other hand, a large

* Strictly *speaking 32° F. should be added*, on account of the different positions of the *in the two scales, but it would not* materially affect the result.

grain powder, in a musket, would evolve its gas so slowly that the b might be expelled with little velocity by the first half of it, and the mainder would be wasted. There is good reason to believe that under the most favourable circumstances, a large proportion of every c of powder is discharged unexploded from the muzzle of the gun, a therefore wasted. In blasting rocks and other mining operations, space within which the powder is confined is absolutely incapable of largement until the gas evolved by the combustion has attained suffi pressure to do the whole work, that is, to rend the rock, for exa asunder. Accordingly, a slowly burning charge will produce the since the rock must give way when the gas attains a certain pre whether that happens in one second or in ten. Indeed, a slowly bur charge is advantageous, as being less liable to shatter the rock or coal, bringing it away in larger masses with less danger. Nitrate of baryt nitrate of soda are sometimes substituted for a part of the nitra potash in mining powder, its combustion being thus retarded.*

When gunpowder is slowly burnt, the products of its decomposition different from those mentioned above; thus, nitric oxide (NO_2), a from incomplete decomposition of the nitre, is perceived in conside quantity, and may be recognised by the red colour produced when brought in contact with air.

The white smoke resulting from the explosion of gunpowder co chiefly of the sulphate and carbonate of potash in a very finely div state; it seems probable that at the instant of explosion they are c verted into vapour, and are afterwards deposited in a state of mi division as the temperature falls. The *fouling* or actual solid residu the gun is very trifling when the powder is dry and has been well in porated; a damp or slowly burning powder leaves, as might be expect the larger residue. The residue always becomes wet on exposure to air, from the great attraction for moisture possessed by the carbonate of potash and sulphide of potassium.

322. *Effect of variations of atmospheric pressure on the combustion of gunpowder.*—From the circumstance that the combustion of gunpowder is independent of any supply of oxygen from the air, it might be supposed that it would be as easily inflamed *in vacuo* as under ordinary atmospheric pressure. This is not found to be the case, however, for a mechanical reason, viz., that the flame from the particles which are first ignited escapes so rapidly into the vacuous space, that it does not inflame the more remote particles. For a similar reason, charges of powder in fuzes are found to burn more slowly under diminished atmospheric pressure, the flame (or heated gas) escaping more rapidly and igniting less of the remaining charge in a given time. It has been determined that if a fuze be charged so as to burn for thirty seconds under ordinary atmospheric pressure (30 inches barometer), each diminution of one inch in barometric pressure will cause a delay of one second in the combustion of the charge, so that the fuze will burn for thirty-one seconds when the barometer stands at 29 inches.

The manufacture of gunpowder may be illustrated by the following experiments on a small scale:—

* Some doubt appears to be thrown upon these principles by the efficiency of nitroglycerine in blasting (*see that compound*).

paration of the ingredients—Charcoal.—A few small pieces of wood are placed ay crucible, which is then filled up with dry nd heated in a moderate fire as long as any rs are evolved, when it may be set aside to

Fig. 264.—Distillation of sulphur.

phur.—500 grains of roll sulphur may be dis- in a Florence flask, using another flask, the of which has been cut off (fig. 264), for a er, from which the sulphur is afterwards d, in a melted state, upon a piece of tin-plate.

re.—1000 grains of impure nitre are dissolved, moderate heat, in four measured ounces of ed water, in an evaporating dish (fig. 265); lution is filtered into a beaker which is placed l water, and stirred with a glass rod until it e cold. The saltpetre flour thus obtained is collected upon a filter, thoroughly d, the filter removed from the funnel, spread out, the saltpetre transferred to r piece of filter paper, and pressed between per to remove as much of the liquid as pos- it is then spread out on paper and dried on a ick. (For the mode of testing its purity see).

Fig. 265.

ture of the ingredients.—60 grains of the char- educed to a very fine powder, 40 grains of the ur, also previously powdered, and 300 grains of ied nitre, are very intimately mixed in a mortar; ains of the mixture are set aside for comparison. ie remainder enough water is added to make o a stiff cake, which is well incorporated under estle for some time. It is then scraped out of ortar and allowed to dry slowly at a very gentle When perfectly dry it is crumbled to a coarse er, and the dust sifted out through a piece of gauze. It will be found instructive to compare, ins and otherwise, the firing of the powder in grains, of the dust, and of the l ingredients without incorporation, observing especially the difference in ty of burning and in the amount of residue.

CHEMISTRY OF FUEL.

3. Several of the applications of chemical principles in the combus- of fuel have been already explained and illustrated. The object of hapter is to compare the chemical composition of the most important ties of fuel, and to exemplify the principles upon which their heating r may be calculated from the results furnished by the analysis of the

l the varieties of ordinary fuel, of course, contain a large proportion rbon, always accompanied by hydrogen and oxygen, and sometimes nall proportions of nitrogen and sulphur. Certain mineral substances lso contained in all solid fuels, and compose the ash when the fuel is .

r all practical purposes it may be stated, that the amount of heat ated by the combustion of a given weight of fuel depends upon the nts of carbon and hydrogen, respectively, which enter into combina- with the oxygen of the air in the act of combustion of the fuel. has been ascertained by experiment that 1 grain of carbon (in the in which it exists in wood charcoal), when combining with oxygen to carbonic acid, produces a quantity of heat which is capable of raising grains of water from 0° to 1° of the Centigrade thermometer. Thi *ally expressed by saying* that the *calorific value of* carbon is 8080

or that carbon produces 8080 *units of heat* during its combustion to carbonic acid. If the fuel, therefore, consisted of pure carbon, it would merely be necessary to multiply its weight by 8080 to ascertain its calorific value.

1 grain of hydrogen, during its conversion into water by combustion, evolves enough heat to raise 34,400 grains of water from 0° C. to 1° C., so that the *calorific value of hydrogen* is 34,400.

If the fuel consisted of carbon and hydrogen only, its calorific value would be calculated by multiplying the weight of the carbon in one grain of the fuel by 8080, and that of the hydrogen by 34,400, when the sum of the products would represent the calorific value. But if the fuel contains oxygen already combined with it, the calorific value will be diminished, since this oxygen will consume a part of the combustible without generating heat, because it already exists in a state of combination with the carbon and hydrogen of the fuel. For example, 1 grain of wood contains 0·5 grain of carbon, 0·06 of hydrogen, and 0·44 of oxygen. Now, oxygen combines with one-eighth of its weight of hydrogen to form water, so that the 0·44 grain of oxygen will convert $\frac{\cdot 44}{8} = \cdot 055$ of the hydrogen into water, without evolution of available heat, leaving only 0·005 available for the production of heat. The calorific value of the wood, therefore, would be represented by the sum of 0·005 × 34,400 (= 172) and 0·5 × 8080 (= 4040), which would amount to 4212; or 1 grain of wood should raise 4212 grains of water from 0° C. to 1° C.

These considerations lead to the following *general formula for calculating the calorific value of a fuel* containing carbon, hydrogen, and oxygen, where c, h, and o respectively represent the carbon, hydrogen, and oxygen in one grain of fuel.

The calorific value (or number of grains of water which might be heated by the fuel from 0° C. to 1° C.) = $8080\ c + 34{,}400 \left(h - \frac{o}{8}\right)$ or $8080\ c + 34{,}400\ h - 4300\ o$.

The calorific value of a fuel, as determined by experiment, is generally less than would be calculated from its chemical composition, in consequence of the absorption of a certain amount of heat attending the chemical decomposition of the fuel. In the case of compounds of carbon and hydrogen, it has been observed that even when they have the same composition in 100 parts, they have not of necessity the same calorific value, the latter being affected by the difference in the arrangement of the component particles of the compound, which causes a difference in the quantity of heat absorbed during its decomposition. Thus olefiant gas (C_4H_4) and cetylene ($C_{32}H_{32}$) have the same percentage composition, and their calculated calorific values would be identical, but the former is found to produce 11,858 units of heat, and the latter only 11,055. As a general rule, however, it is found that the calorific values of the hydrocarbons which contain an equal number of equivalents of each element, agree more nearly with the calculated numbers than do those of hydrocarbons which contain an unequal number of equivalents, like marsh-gas (C_2H_4).

It must be remembered that the calorific value of a fuel represents the actual amount of heat which a given weight of it is capable of producing, and is quite independent of the manner in which the fuel is burnt. Thus, hundredweight of coal will produce precisely the same amount of heat in ordinary grate as in a wind-furnace, though in the former case the lar

scarcely be capable of melting copper, and in the latter it will melt . The difference resides in the *temperature* or *calorific intensity* of two fires; in the wind-furnace, through which a rapid draught of air aintained by a chimney, a much greater weight of atmospheric oxygen rought into contact with the fuel in a given time, so that, *in that* , a greater weight of fuel will be consumed and more heat will be luced; hence the fire will have a higher temperature, for the tem- ture represents, not the quantity of heat present in a given mass of er, but the intensity, or extent to which that heat is accumulated at particular point. In the case of the wind-furnace here cited, a further ntage is gained from the circumstance, that the rapid draught of air rs a given weight of fuel to be consumed in a smaller space, and, of se, the smaller the area over which a given quantity of heat is distri- d, the higher the temperature within that area (as exemplified in the of the common burning-glass). In some of the practical applications el, such as heating steam-boilers and warming buildings, it is the *ific value* of the fuel which chiefly concerns us, but the case is different re metals are to be melted, or chemical changes to be brought about he application of a very high temperature, for it is then the *calorific sity*, or actual temperature of the burning mass, which has to be con- ed. No trustworthy method has yet been devised for determining lirect experiment the calorific intensity of fuel, and it is therefore tained by calculation from the calorific value.

et it be required to calculate the calorific intensity, or actual tempera- , of carbon burning in pure oxygen gas.

grains (1 eq.) of carbon combine with 16 grains (2 eqs.) of oxygen, ucing 22 grains of carbonic acid; hence 1 grain of carbon combines 2·67 grains of oxygen, producing 3·67 grains of carbonic acid. It been seen above that 1 grain of carbon evolves 8080 units of heat, or pable of raising 8080 grains of water from 0° to 1°C., or, on the sup- tion that the water would bear such an elevation of temperature, the ain of carbon would raise 1 grain of water from 0° to 8080° C. If *pecific heat* (or heat required to raise 1 grain through 1°, *see* p. 426) of onic acid were the same as that of water, 8080° divided by 3·67 ld represent the temperature to which the 3·67 grains of carbonic acid ld be raised, and therefore the temperature to which the solid carbon lucing it would be raised in the act of combustion. But the specific of carbonic acid gas is only 0·2163, so that a given amount of heat ld raise 1 grain of carbonic acid to nearly five times as high a tem- ture as that to which it would raise 1 grain of water.

ividing the 8080 units of heat (available for raising the temperature he carbonic acid) by 0·2163, the quantity of heat required to raise 1 n of carbonic acid 1°, we obtain 37,355 for the number of degrees ugh which 1 grain of carbonic acid might be raised by the combustion grain of carbon. But there are 3·67 grains of carbonic acid formed he combustion, so that the above number of degrees must be divided ·67 in order to obtain the actual temperature of the carbonic acid at instant of its production, that is, the temperature of the burning mass.

calorific intensity of carbon burning in pure oxygen is, therefore, 355° C. ÷ 3·67 =) 10,178° C. or 18,352° F. But if the carbon be nt in air, the temperature will be far lower, because the nitrogen of air will absorb a part of the heat, to which it contributes nothing. 2·67 grains of oxygen required to burn 1 grain of carbon would be

mixed, in air, with 8·93 grains of nitrogen, so that the 8080 units of heat would be distributed over 3·67 grains of carbonic acid and 8·93 grains of nitrogen. Since the specific heat of carbonic acid is 0·2163, the product of 3·67 × 0·2163 (or 0·794) represents the quantity of heat required to raise the 3·67 grains of carbonic acid from 0° to 1° C.

The specific heat of nitrogen is 0·2438; hence 8·93 × 0·2438 (or 2·177) represents the quantity of heat required to raise the 8·93 grains of atmospheric nitrogen from 0° to 1° C.

Adding together these products, we find that 0·794 + 2·177 = 2·971 represents the quantity of heat required to raise both the nitrogen and carbonic acid from 0° to 1° C.

Dividing the 8080° by 2·971, we obtain 2720° C. (4928° F.) for the number of degrees through which these gases would be raised in the combustion, *i.e.*, for the calorific intensity of carbon burning in air. By heating the air before it enters the furnace (as in the hot blast iron furnace), of course the calorific intensity would be increased; thus if the air be introduced into the furnace at a temperature of 600° F., it might be stated, without serious error, that the temperature producible in the furnace would be 5528° F. (4928° + 600°). The temperature might be further increased by diminishing the area of combustion, as by employing very compact fuel and increasing the pressure of the blast.

In calculating the calorific intensity of hydrogen burning in air, from its calorific value, it must be remembered that in the experimental determination of the latter number the steam produced in the combustion was condensed to the liquid form, so that its latent heat was added to the number representing the calorific value of the hydrogen; but the latent heat of the steam must be *deducted* in calculating the calorific intensity, because the steam goes off from the burning mass and carries its latent heat with it.

1 grain of hydrogen, burning in air, combines with 8 grains of oxygen, producing 9 grains of steam, leaving 26·77 grains of atmospheric nitrogen, and evolving 34,400 units of heat.

It has been experimentally determined that the latent heat of steam is 537° C., that is, 1 grain of water, in becoming steam, absorbs 537 units of heat (or as much heat as would raise 537 grains of water from 0° to 1° C.) without rising in temperature as indicated by the thermometer. The 9 grains of water produced by the combustion of 1 grain of hydrogen will absorb, or render latent, 537 × 9 = 4833 units of heat. Deducting this quantity from the 34,400 units evolved in the combustion of 1 grain of hydrogen, there remain 29,567 units of heat available for raising the temperature of the 9 grains of steam and 26·77 grains of atmospheric nitrogen. The specific heat of steam being 0·480, the number (0·480 × 9 =) 4·32 represents the quantity of heat required to raise the 9 grains of steam through 1° C.; and the specific heat of nitrogen (0·2438) multiplied by its weight (26·77 grains), gives 6·53 units of heat required to raise the 26·77 grains of nitrogen through 1° C. By dividing the available heat (29,567 units) by the joint quantities required to raise the steam and nitrogen through 1° C. (4·32 + 6·53 = 10·85), we obtain the number 2725° C. (4937° F.) for the calorific intensity of hydrogen burning in air.

The method of calculating the calorific intensity of a fuel composed of carbon, hydrogen, and oxygen, will now be easily followed.

Let c and h respectively represent the weights of carbon and hydrogen in 1 lb.

l, and o that of the oxygen. Then $\frac{o}{8}$ = weight of hydrogen required to convert xygen into water, and $h - \frac{o}{8}$ represents the hydrogen which is available for the ction of heat.

$$8080\,c + 34{,}400\left(h - \frac{o}{8}\right) \text{ represents the}$$

calorific value in °C., $= 8080\,c + 34{,}400\,h - 4300\,o$.

c = atmospheric oxygen consumed by the carbon;

$\left(h - \frac{o}{8}\right)$ or $8\,h - o$ = atmospheric oxygen consumed by the hydrogen available el.

4 $(2{\cdot}67\,c + 8\,h - o)$ = atmospheric nitrogen $= 8{\cdot}92\,c + 26{\cdot}72\,h - 3{\cdot}34\,o$. ltiplying this by the specific heat of nitrogen 0·2438, we obtain—

$c + 6{\cdot}51\,h - 0{\cdot}81\,o$ for the heat required to raise the nitrogen through 1° C.

94 c represents the quantity of heat required to raise the carbonic acid through , and $4{\cdot}32\,h$ is the heat required to raise the steam through 1°. Accordingly, vailable heat, $8080\,c + 34{,}400\,h - 4300\,o$, must be divided by $0{\cdot}794\,c + 4{\cdot}32\,h$ $17\,c + 6{\cdot}51\,h - 0{\cdot}81\,o$), or $2{\cdot}96\,c + 10{\cdot}83\,h - 0{\cdot}81\,o$ in order to obtain the fic intensity.

nce, the calorific intensity, in Centigrade degrees, of a fuel composed of carbon, gen, and oxygen, is represented by the formula—

$$\frac{8080\,c + 34{,}400\,h - 4300\,o}{2{\cdot}96\,c + 10{\cdot}83\,h - 0{\cdot}81\,o}.$$

e actual calorific intensity of the fuel is not so high as it should be ding to theory, because a part of the carbon and hydrogen is con- d into gas by destructive distillation of the fuel, and this gas is not lly burnt *in the fire*, so that its calorific intensity is not added to of the burning solid mass. Again, a portion of the carbon is con- d into carbonic oxide (CO), especially if the supply of air be imperfect, much less heat is produced than if the carbon were converted into nic acid; although it is true that this carbonic oxide may be con- d above the fire by supplying air to it, the heat thus produced does ncrease the calorific intensity or temperature of the fire itself.

e grain of carbon furnishes 2·33 grains of carbonic oxide. These 2·33 s of carbonic oxide evolve, in their combustion, 5599 units of heat. f the 1 grain of carbon had been converted at once into carbonic it would have evolved 8080 units of heat, so that 8080 − 5599, or , represents the heat evolved during the conversion of 1 grain of n into carbonic oxide, showing that a considerable loss of heat *in the* s caused by an imperfect supply of air. It has been already pointed n the section relating to Coal, that the formation of carbonic oxide is imes encouraged with a view to the production of a flame from non- ng coal, such as anthracite.

e table (p. 434) exhibits the average percentage composition of the ipal varieties of fuel (exclusive of ash), together with their calculated fic values and intensities.

all ordinary fires and furnaces, a large amount of heat is wasted in urrent of heated products of combustion escaping from the chimney. ourse, a portion of this heat is necessary in order to produce the ht of the chimney. In boiler furnaces it is found that, for this pur- the temperature of the air escaping from the chimney must not be *than from 500° to 600° F.* If the fuel could be consumed by sup-

plying only so much air as contains the requisite quantity of oxygen, a great saving might be effected, but in practice, about twice the calculated quantity of air must be supplied, in order to effect the removal of the products of combustion with sufficient rapidity.

Much economy of fuel may be expected from the use of furnaces constructed on the principle of Siemens' *regenerative furnace*, in which the waste heat of the products of combustion is absorbed by a quantity of fire-bricks, and employed to heat the air before it enters the furnace, two chambers of fire-bricks doing duty alternately, for absorbing the heat from the issuing gas, and for imparting heat to the entering air, the current being reversed by a valve as soon as the fire-bricks are strongly heated.

	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Sulphur.	Calorific Value.—Intensity.	
Wood (Oak), .	50·18	6·08	43·74	...	...	4212°C.	2380°C.
Peat, ...	61·53	5·64	32·82	...	...	5654	2547
Lignite (Bovey)	67·86	5 75	23·39	0·57	2·41	6569	2628
Bituminous coal,	79·38	5·34	13·01	1·85	0·39	7544	2694
Charcoal, . . .	90·44	2·91	6·63	...	...	8003	2760
Anthracite, . .	91·86	3·33	3·02	0·84	0 92	8337	2779
Coke, ...	97·32	0·49	2·17			8009	2761

(For the principles of smoke prevention, and other particulars of the chemistry of fuel, *see* Coal.)

ORGANIC CHEMISTRY.

24. Although it is impossible to propose a definition of the term *nic substance* which shall not be applicable to some of the substances monly regarded as *inorganic*, it is found advantageous for the purposes udy to treat *organic chemistry* as a separate division of the science, ing especially with those substances which are usually obtained, er directly or indirectly, from animals and vegetables.

ne very important distinction between organic and inorganic substances hat the former are for the most part composed of carbon, hydrogen, ogen, and oxygen, in different proportions and in various modes of ngement, and that they are, therefore, much more frequently con- ible into each other by metamorphosis, without extraneous addition natter, than inorganic substances are.

t has been already pointed out (p. 83) that the chemist is gradually ning to produce, though by somewhat clumsy and circuitous processes, ny of the substances which were formerly believed incapable of being ned, except through the intervention of life; but no substance possess- an *organised structure*, such as woody fibre or muscular fibre, and no olutely indispensable constituent of animal or vegetable frames, if we ept water, has yet been artificially procured.

t will not escape notice that the four elements which compose the ater number of organic substances, viz., hydrogen, oxygen, nitrogen, carbon, are, respectively, monatomic, diatomic, triatomic, and tetratomic nents (p. 151), and are, therefore, capable of forming a greater variety compounds than would be the case if they were elements of equal nicities.

n the following pages, no strictly scientific classification of organic stances has been adopted, since it would often render it necessary to cribe, in separate sections, substances which are, in nature, closely con- ed with each other, but an empirical arrangement has been followed, hat the reader may find his memory assisted and the interest of the ject sustained, by being enabled to bring the facts and explanations immediate connection with familiar processes of ordinary life.*

ne of the most conspicuous substances standing upon the boundary veen organic and inorganic chemistry is the compound of carbon and ogen known as *cyanogen*, which is intimately connected with inorganic stances through some of the processes for its production, and through similarity to the chlorine group of elements, whilst the origin and

*The number of organic substances known to the chemist is so great that a mere list of would occupy a volume. In the present work a selection has been made of those h are interesting for their practical applications or instructive from theoretical con- itions.

chemical properties of a large number of its compounds give them a claim to be ranked among organic substances. The study of this substance, therefore, will form a fit introduction to organic chemistry.

CYANOGEN AND ITS COMPOUNDS.

325. In the beginning of the last century, a manufacturer of colours at Berlin accidentally obtained a blue powder when precipitating sulphate of iron with potash. This substance was used as a colour, under the name of *Prussian blue*, for several years, before any explanation of its production was attempted, or even before the conditions under which it was formed were exactly determined. In 1824 it was shown that Prussian blue could be prepared by calcining dried animal matters with carbonate of potash and mixing the aqueous solution of the calcined mass, first with sulphate of iron and afterwards with hydrochloric acid; but the most important step towards the determination of its composition was made by Macquer, who found that by boiling it with an alkali, Prussian blue was decomposed, yielding a residue of red oxide of iron, and a solution which reproduced the blue when mixed with a salt of iron, from which he inferred that the colour was a compound of the oxide of iron with an acid for which the alkali had a more powerful attraction,—a belief confirmed, in 1782, by Scheele's observation, that when an alkaline solution prepared for making the blue was exposed to the air, or to the action of carbonic acid, it lost the power of furnishing the colour, but the escaping vapour struck blue on paper impregnated with oxide of iron. Scheele also prepared the acid in a pure state, and it soon after obtained the name of *prussic acid*.

In 1787 Berthollet found prussic acid to be composed of carbon, hydrogen, and nitrogen, but he also showed that the power of the alkaline liquor to produce Prussian blue depended upon the presence of a yellow salt crystallising in octahedra, and containing prussic acid, potash, and oxide of iron, though the latter was so intimately bound up with the other constituents, that it could not be separated by those substances which are usually employed to precipitate iron.

Porrett, in 1814, applying the greatly increased resources of chemistry to the investigation of this subject, decomposed Prussian blue with baryta, and subsequently removed the baryta from the salt thus obtained by means of sulphuric acid, when he obtained a solution of the acid, which he named *ferruretted chyazic acid*.

In 1815, Gay-Lussac, having boiled Prussian blue (or prussiate of iron as it was then called) with red oxide of mercury and water, and crystallised the so-called prussiate of mercury, exposed it, in the dry state, to the action of heat, and obtained a gas, having the composition C_2N, which was called *cyanogen*,* in allusion to its connection with Prussian blue. It was then seen that the substance which had been called ferruretted chyazic acid contained iron and the elements of cyanogen, whence it was called *ferrocyanic acid*, and its salts were spoken of as ferrocyanates. Robiquet first obtained this acid in the crystallised state, having the composition $C_6H_2N_3Fe$; and since it was found that, when brought in contact with metallic oxides, it exchanged the H_2 for two equivalents of the metal according to the equation—

$$H_2.C_6N_3Fe + 2MO = M_2.C_6N_3Fe + 2HO$$

* From κυάνεος, blue.

concluded that the C_6N_3Fe composed a distinct group or radical, was named *ferrocyanogen*, the acid being called *hydroferrocyanic* and the salts *ferrocyanides.*

. *Prussiate of potash.*—The yellow prussiate of potash or *fer-nide of potassium* ($K_2.C_6N_3Fe + 3Aq.$), is manufactured upon a scale by a process which is the more interesting because it turns to nt some of the commonest kinds of refuse, such as old leather, hoof gs, blood, and, in short, any animal matter rich in nitrogen, and not cable to any more economical purpose. Sometimes these substances rst subjected to destructive distillation for the carbonate of ammonia they are capable of yielding, and the residual highly nitrogenised oal is then used for the production of the ferrocyanide of potassium. matters are fused in an iron vessel with carbonate of potash and iron s, and the fused mass is heated with water in open boilers, when a y solution is obtained, which, after evaporation, deposits truncated nidal crystals of ferrocyanide of potassium, containing 3 equivalents ter.

e theory of this process has been elucidated by the researches of g. If carbonate of potash be strongly heated in contact with carbon, there result (page 260) carbonic oxide and potassium, $CO_2 + C_2 = 3CO + K$; but if the carbon be associated with nitrogen, duction will be effected at a much lower temperature, and the potas- will combine with 2 equivalents of carbon and 1 equivalent of gen, to form the *cyanide of potassium* (KC_2N). When this salt, dis- l in water, is heated with metallic iron in the presence of air, oxygen orbed, and the iron dissolved to form ferrocyanide of potassium—

$$3KC_2N + Fe + O = K_2.C_6N_3Fe + KO.$$

xygen may also be acquired from the water, an equivalent quantity drogen being evolved.

ussian blue.—For the preparation of Prussian blue it is usual to olutions of ferrocyanide of potassium and persulphate of iron, when lue is precipitated, having been produced according to the equation—

$$\underset{\text{Ferrocyanide of potassium.}}{3K_2Fcy} + 2(Fe_2O_3.3SO_3) = 6(KO.SO_3) + \underset{\text{Prussian blue.}}{Fe_4Fcy_3}$$

hich the symbol Fcy represents the group C_6N_3Fe (*ferrocyanogen*), is capable of playing the same part in many decompositions as if re an elementary substance. This compound radical has never yet obtained in the separate state, but it can be traced through a com- series of compounds, in which it exactly resembles chlorine in its ical relations; thus the *hydroferrocyanic acid* (H_2Fcy), and the fer- nides of the metals (M_2Fcy), are perfectly analogous to hydrochloric nd the chlorides, though containing a compound radical instead of a e one; but whereas chlorine is a monobasic or monatomic radical, ining only with 1 equivalent of hydrogen or a metal, ferrocyanogen asic or di-atomic; and hence Prussian blue, the *sesquiferrocyanide of* corresponding to the sesquioxide (Fe_2O_3), has the composition Fy_3, whilst the sesquichloride is Fe_2Cl_3. When Prussian blue is pre- by pouring solution of persulphate of iron into an excess of ferro- de of potassium, it is found that, as soon as the excess of the latter *as been washed away, the* precipitate dissolves in pure water, form-

ing what is used by dyers under the name of *soluble Prussian blue*. Oxalic acid is capable of dissolving the blue, and this solution forms the basis of ordinary blue ink.

Prussian blue is sometimes prepared with the green protosulphate of iron ($FeO.SO_3$), but in that case it is necessary to expose the precipitate for some time to the air, since the first result is a nearly white precipitate, which may be regarded as a double ferrocyanide of iron and potassium (K_2Fcy, Fe_2Fcy).

$$2(K_2Fcy) + 2(FeO.SO_3) = 2(KO.SO_3) + K_2Fcy, Fe_2Fcy.$$

When this precipitate is exposed to the air, it gradually acquires a dark-blue colour, becoming eventually converted into Prussian blue by oxidation—

$$3(K_2Fcy.Fe_2Fcy) + O_3 = 3K_2Fcy + Fe_2O_3 + Fe_4Fcy_3.$$

Prussian blue is easily decomposed by alkalies, a brown residue of sesquioxide of iron being left, $Fe_4Fcy_3 + 6KO = 3K_2Fcy + 2Fe_2O_3$. This decomposition is turned to account by the calico-printer for producing a buff or white pattern upon a blue ground. The stuff having been dyed blue by passing, first through a solution of a per-salt of iron, and afterwards through one of ferrocyanide of potassium, the pattern is discharged by an alkali, which leaves the brown peroxide of iron capable of being removed by a dilute acid, when the stuff has been rinsed, so as to leave the design white.

Hydroferrocyanic acid.—By decomposing a cold saturated solution of the ferrocyanide of potassium with about an equal volume of hydrochloric acid, colourless crystals of *hydroferrocyanic acid* (H_2Fcy) are obtained, which are insoluble in hydrochloric acid, but readily soluble in water. When a solution of this acid is heated, it evolves hydrocyanic acid (HC_2N), and deposits a white precipitate of cyanide of iron (FeC_2N), which becomes blue on exposure to the air, being converted into Prussian blue; the simplest way of explaining this, as well as many other decompositions of hydroferrocyanic acid and the ferrocyanides, is to view the radical ferrocyanogen as formed by the union of three equivalents of cyanogen (C_2N) and one equivalent of iron, when hydroferrocyanic acid becomes $H_2.Cy_3Fe$, and Prussian blue $Fe_4.3Cy_3Fe$.*

The decomposition of the hydroferrocyanic acid by heat would then be represented by the equation—

$$\underset{\text{Hydroferrocyanic acid.}}{H_2.Cy_3Fe} = \underset{\text{Hydrocyanic acid.}}{2HCy} + \underset{\text{Protocyanide of iron.}}{FeCy}$$

and the formation of Prussian blue from this last compound on exposure to air—

$$9FeCy + O_3 = \underset{\text{Prussian blue.}}{Fe_4.3Cy_3Fe} + Fe_2O_3.$$

Hydrocyanic or *prussic acid.*—Advantage is taken of the decomposition of the ferrocyanide of potassium by acids, in the preparation of solution of hydrocyanic acid for medicinal use. For this purpose, 2 parts of the ferrocyanide of potassium in powder are distilled with 1½ parts of oil of vitriol diluted with 2 parts of water, the vapour of hydrocyanic acid

* Since Cy requires one equivalent of hydrogen or a metal to saturate its combining power, Cy_3 would require three equivalents, so that Cy_3Fe would still be capable of receiving six equivalents of a metal, and hence the ferrocyanide of potassium is $Cy_3Fe.K_4$. In Prussian blue the four equivalents of iron represent six equivalents of hydrogen or potassium exactly as in $2Fe_2Cl_3$ or Fe_4Cl_6.

ng carefully condensed (*see* fig. 45). The change is represented by equation—

$$K_2(Cy_3Fe) + 3(HO.SO_3) = 3(KO.SO_3) + KFe(Cy_3Fe) + 3HCy.$$

rocyanide of potassium. Ferrocyanide of iron and potassium. Hydrocyanic acid.

ere is left in the retort a pale greenish salt, which rapidly becomes blue en exposed to the air, and is probably identical with the double fercyanide of potassium and iron produced when protosulphate of iron is composed by ferrocyanide of potassium (p. 438).

The solution of hydrocyanic acid thus obtained is colourless, and hales the remarkable odour of the acid; its acid characters are very ble indeed, even more so than those of carbonic acid, but it is extremely sonous, a very small dose destroying life almost immediately. Hydronic acid is found in laurel-water, and in water distilled from the kernels many stone-fruits, such as the peach, apricot, plum. In minute doses drocyanic acid is a very valuable remedy, and is employed in medicine solutions of different strengths. One of these, which is known as the d of the London Pharmacopœia, contains 2 per cent. of hydrocyanic d, and is prepared by the process mentioned above. *Scheele's acid* ies in strength, but usually contains between 4 and 5 per cent. of true drocyanic acid. This acid is prepared from Prussian blue, by the cess originally employed by Scheele when the acid was discovered. consists in boiling Prussian blue with water and red oxide of mercury, til the blue colour disappears; peroxide of iron is separated, and anide of mercury (HgCy) passes into solution; the latter is filtered, xed with diluted sulphuric acid, and shaken with iron-filings, which ecipitate the mercury in the metallic state, leaving free hydrocyanic id in the liquid, which is then distilled—

$$HgCy + Fe + HO.SO_3 = HCy + FeO.SO_3 + Hg.$$

order clearly to understand this process, it must be known that the rcury exhibits a special tendency to combine with cyanogen, which is ficiently powerful, in this instance, to bring about the decomposition the ferrocyanogen existing in the Prussian blue, a part of the cyanogen ng exchanged for the oxygen of the oxide of mercury.

It is from the *cyanide of mercury* that the pure anhydrous hydrocyanic d and cyanogen itself are prepared. For these purposes, it may be obned by dissolving the red oxide of mercury in hydrocyanic acid, when louble decomposition takes place, exactly as with hydrochloric acid, O + HCy = HgCy + HO, and the cyanide of mercury is obned in square prismatic crystals on evaporating the solution. If se crystals be dried and gently warmed with strong hydrochloric d, chloride of mercury will be formed, and hydrocyanic acid evolved, Cy + HCl = HgCl + HCy. The mixed vapours of hydrochloric and drocyanic acid are passed over fragments of marble ($CaO.CO_2$), which orb the hydrochloric acid ($CaO.CO_2 + HCl = CaCl + HO + CO_2$), not the hydrocyanic, since the latter is too weak an acid even to place carbonic acid. The mixture of hydrocyanic and carbonic acids passed over chloride of calcium to remove aqueous vapour, and afterrds through a tube cooled in a mixture of ice and salt, when the drocyanic acid is condensed to a colourless liquid, which evaporates rapidly when exposed to the air that it lowers the temperature to *freezing point of the acid*, which is about 0° F.; at a little

above the ordinary temperature (79° F.) it boils, and emits a vapour which burns with a blue flame. When kept for some time it is liable to undergo a spontaneous decomposition, evolving ammonia, and being converted into a brown mass of uncertain composition. The aqueous solution of the acid suffers a similar change, and since exposure to light favours the decomposition, the medicinal acid is usually kept in bottles covered with paper. The presence of a very small quantity of sulphuric acid prevents this change, and hence the acid prepared by distilling ferrocyanide of potassium with sulphuric acid, which usually contains traces of the latter, can be preserved much better than that prepared by other methods.

When hydriodic acid gas is passed into anhydrous hydrocyanic acid cooled by ice a crystalline body is formed, which has the composition $HC_2N . HI$. It is readily soluble in water and alcohol, but not in ether, and may be sublimed with little decomposition. This substance is not acid, and does not answer to the tests for hydrocyanic acid. When decomposed by potash, it gives ammonia, formiate of potash, and iodide of potassium, so that it may be regarded as the hydriodate of an ammonia formed by the substitution of one equivalent of the triatomic radical formyle (C_2H) for the three equivalents of hydrogen; or *hydriodate of formylamine* $N(C_2H)''' . HI$.

327. *Cyanogen* itself (C_2N) can be prepared by the mere action of heat upon the cyanide of mercury (in a test-tube provided with a glass jet for burning the gas, fig. 266). This salt resolves itself into metallic mercury, cyanogen, and a brown substance which has been called *paracyanogen* (C_2N_2), and appears to have been formed by the union of three equivalents of cyanogen. Cyanogen gas is easily distinguished from all others by its peculiar odour and its property of burning with a fine peach-coloured flame. Being nearly twice as heavy as air (sp. g. 1·8), it may be collected by downward displacement, for water dissolves about four times its volume of the gas, yielding a solution which is prone to undergo a spontaneous decomposition remarkable for the comparatively complex products which it furnishes, amongst which we trace the oxalate ($NH_4O . C_2O_3$) and formiate ($NH_4O . C_2HO_3$) of ammonia, and urea ($C_2H_4N_2O_2$), all derived, be it remembered, from the elements of cyanogen and water. In its chemical relations cyanogen presents a striking resemblance to chlorine. Thus, at a slightly elevated temperature, potassium and sodium take fire in it, forming the cyanides of those metals precisely as the chlorides would be formed. Again, when cyanogen is absorbed by a solution of potash, the cyanide of potassium and cyanate of potash are formed—

Fig. 266.

$$2KO + Cy_2 = \underset{\text{Cyanate of potash.}}{KO . CyO} + \underset{\text{Cyanide of potassium.}}{KCy}$$

just as the chloride of potassium and hypochlorite of potash result from the action of chlorine upon potash, $2KO + Cl_2 = KO . ClO + KCl$. A pressure of about 4 atmospheres is required to liquefy cyanogen, when it forms a colourless liquid of sp. gr. 0·87, freezing to a crystalline mass at − 30° F.

Cyanide of potassium.—The most useful of the cyanides is the cyanide of potassium, which is extensively employed in electro-plating and gilding. This salt may be formed by a very interesting process, which in one of

e few in which the atmospheric nitrogen takes part, and consists in ssing air over red-hot charcoal which has been previously soaked in a rong solution of carbonate of potash and dried, when the nitrogen requi- te for the formation of the cyanide is absorbed from the air, and carbonic xide is disengaged—

$$KO.CO_2 + C_4 + N = \underset{\text{Cyanide of potassium.}}{KC_2N} + 3CO.$$

It is probably by a similar change that the cyanide of potassium is pro- uced in the blast-furnaces (page 305) in which iron ores are reduced, he potash being derived from the ash of the fuel. The cyanide is always repared for use from the ferrocyanide, which is resolved by a very high emperature into cyanide of potassium and carbide of iron, with evolution f nitrogen—

$$\underset{\substack{\text{Ferrocyanide}\\\text{of potassium.}}}{K_2Cy_3Fe} = \underset{\substack{\text{Cyanide of}\\\text{potassium.}}}{2KCy} + FeC_2 + N.$$

In order to avoid the loss of the third equivalent of cyanogen, it is usual fuse the ferrocyanide with carbonate of potash in the proportion of 3 rts of the dry carbonate to 7 parts of the dried ferrocyanide; the mixture fused in a covered earthen crucible, and occasionally stirred until gas ases to be evolved; the crucible is then removed from the fire, allowed stand for a minute or two that the metallic iron may subside, and the ear fused cyanide poured out on to a stone. The change involved in this ocess is represented by the following equation—

$$2K_2Cy_3Fe + 2(KO.CO_2) = 5KCy + \underset{\text{Cyanate of potash.}}{KO.CyO} + Fe_2 + 2CO_2$$

hence it will be seen that the commercial cyanide of potassium is con- minated with cyanate of potash. It also contains a considerable quan- y of carbonate of potash, so that the proportion of cyanide is often only per cent. The white porcelain-like masses of cyanide of potassium liquesce when exposed to the air, and emit the odour of hydrocyanic acid well as that of ammonia; the former is disengaged from the cyanide by e action of the atmospheric carbonic acid, whilst the ammoniacal odour due to the carbonate of ammonia produced by the action of moisture on the cyanate of potash—

$$\underset{\text{Cyanate of potash.}}{KO.C_2NO} + 4HO = KO.CO_2 + NH_4O.CO_2.$$

Pure cyanide of potassium is deposited in colourless cubical crystals hen vapour of hydrocyanic acid is passed into an alcoholic solution of otash, or it may be obtained by boiling the commercial cyanide with cohol and filtering while hot, when the cyanide crystallises out as the lution cools.

The use of cyanide of potassium in electroplating and gilding depends pon the power of a solution of the salt to dissolve the cyanides of gold nd silver, forming compounds which are easily decomposed by the gal- anic current, with deposition of metallic gold or silver upon any object apable of conducting the current, which may be attached to the negative ole (p. 363). Solution of cyanide of potassium is also able to dissolve etallic silver and sulphide of silver, which is taken advantage of in emoving photographic stains from the hands and in cleaning silver or *old lace*.

At a high temperature, cyanide of potassium is a very powerful reducing agent, abstracting two equivalents of oxygen from most of the metallic oxides, so as to liberate the metals, being itself converted into cyanate of potash. Thus, when the binoxide of tin is fused with cyanide of potassium, $SnO_2 + KCy = Sn + KO.CyO$. This property of the cyanide is often applied in chemical experiments. The cyanate of potash is readily distinguished by the peculiar pungent odour of cyanic acid, which it emits when treated with dilute sulphuric acid, though the greater part of the cyanic acid is decomposed with effervescence, yielding sulphate of ammonia and carbonic acid—

$$KO.C_2NO + 2(HO.SO_3) + 2HO = KO.SO_3 + NH_4O.SO_3 + 2CO_2.$$

When fused cyanate of potash is triturated with dried oxalic acid, and the mass treated with water, a white insoluble substance is left, which has been called *cyamelide*, and has the composition C_2HNO_2, being *metameric* with hydrated cyanic acid, $HO.C_2NO$; when this substance is distilled, hydrated cyanic acid passes over as a colourless liquid, which can only be preserved at a very low temperature, for if the receiver containing it be removed from the freezing mixture employed to condense the cyanic acid, the latter becomes hot and turbid, soon begins to boil violently, and is converted into a white mass of cyamelide resembling porcelain.

Cyanide of potassium when fused with sulphur, forms a compound corresponding to cyanate of potash, but containing sulphur in place of oxygen, and having the formula KS, CyS, which is commonly spoken of as *sulphocyanide of potassium*, being represented as containing a compound radical, *sulphocyanogen* $CyS_2 = Scy$. The sulphocyanide of potassium is generally prepared by fusing 3 parts of dried ferrocyanide of potassium and 1 part of carbonate of potash (the materials for making cyanide of potassium) with 2 parts of sulphur, in a covered crucible. By washing the cooled mass with boiling water, the sulphocyanide is extracted, and may be obtained by evaporating the solution, in prismatic crystals resembling nitre. By decomposing the sulphocyanide of potassium with acetate of lead, the sulphocyanide of lead ($PbCyS_2$) is obtained, and this, when acted upon with sulphuretted hydrogen, yields sulphide of lead and *hydrosulphocyanic acid*, $HCyS_2$, the latter being a colourless oily liquid which may be crystallised by cold. This acid is remarkable for the dark red colour (due to sulphocyanide of iron) which it gives with the per-salts of iron, for which sulphocyanide of potassium is frequently employed as a test. A very delicate test (Liebig's test) for hydrocyanic acid in cases of poisoning is also founded upon that circumstance, for if a watch-glass moistened with yellow sulphide of ammonium (p. 272) be exposed to the action of vapour of hydrocyanic acid, the latter is absorbed and converted into sulphocyanide of ammonium—

$$\underset{\text{Yellow sulphide of ammonium.}}{NH_4S} + S_2 + HCy = \underset{\text{Sulphocyanide of ammonium.}}{NH_4CyS_2} + HS$$

by applying a gentle heat to the watch-glass, any excess of sulphide of ammonium is volatilised, and a drop of perchloride of iron will then give the blood-red colour with the sulphocyanide.

[illegible]8. *Ferricyanide of potassium.*—When chlorine is passed into a solu[illegible] f ferrocyanide of potassium, the liquid assumes a brown colour, and, [illegible]vaporated, deposits beautiful red rhombic prisms, which are found,

analysis, to have the composition $K_3Cy_6Fe_2$, having been formed from the ferrocyanide according to the equation—

$$\underset{\text{Ferrocyanide of potassium.}}{2K_2Cy_3Fe} + Cl = \underset{\text{Ferricyanide of potassium.}}{K_3Cy_6Fe_2} + KCl .$$

This salt is known as *red prussiate of potash*, or ferricyanide of potassium, and is used in dyeing; for if a piece of stuff be heated in a solution of the ferricyanide acidulated with acetic acid, a blue compound similar to Prussian blue is deposited in the fibre.

Ferricyanide of potassium is also employed for the preparation of *Turnbull's blue* (ferricyanide of iron), which is precipitated when a solution of that salt is mixed with one of sulphate of iron.

$$3(FeO . SO_3) + \underset{\text{Ferricyanide of potassium.}}{K_3(Cy_6Fe_2)} = 3(KO . SO_3) + \underset{\text{Ferricyanide of iron.}}{Fe_3(Cy_6Fe_2)} .$$

In calico-printing, a mixture of the ferricyanide of potassium with potash is employed as a discharge for indigo, such a mixture acting as a powerful bleaching agent, in consequence of its tendency to impart oxygen to any substance in need of that element, the ferricyanide being converted into the ferrocyanide; thus—

$$\underset{\text{Ferricyanide of potassium.}}{K_3(Cy_6Fe_2)} + KO = \underset{\text{Ferrocyanide of potassium.}}{2K_2Cy_3Fe} + O .$$

The ferricyanide of potassium is assumed to contain a compound radical, *ferricyanogen* (Cy_6Fe_2), which represents a double equivalent of ferrocyanogen (Cy_3Fe).* The *hydroferricyanic acid* ($H_3Cy_6Fe_2$) can be obtained in a crystallised state, and many of the corresponding ferricyanides have been examined.

Ferrocyanogen and ferricyanogen are not the only compound radicals of this description; there are *cobalticyanogen* (Cy_6Co_2), *manganicyanogen* (Cy_6Mn_2), *chromicyanogen* (Cy_6Cr_2), *platinocyanogen* (Cy_2Pt), *palladiocyanogen* (Cy_2Pd), and *iridiocyanogen* (Cy_3Ir), but none of these have received any useful applications. The platinocyanides are remarkable for their brilliant colours.

329. *Chlorides of cyanogen.*—When moist cyanide of mercury is shaken up in a bottle of chlorine gas, and set aside for some time in a dark place, the yellow colour of the chlorine disappears, and the bottle is filled with a colourless gas having a remarkably pungent and tear-exciting odour; this is the *gaseous chloride of cyanogen* (CyCl); $HgCy + Cl_2 = HgCl + CyCl$. If light have access during this experiment, an oily *liquid chloride of cyanogen*, Cy_2Cl_2, is produced.

The chloride of cyanogen gas may be liquefied by a pressure of four atmospheres, and if the liquid is kept for some days in a sealed tube, it is converted into a white mass of *solid chloride of cyanogen*, Cy_3Cl_3. When this is acted on by water, it yields *cyanuric acid*, $3HO . Cy_3O_3$, according to the equation $Cy_3Cl_3 + 6HO = 3HCl + 3HO . Cy_3O_3$. This acid is very interesting on account of its polymeric relation to cyanic acid ($HO . CyO$), which may be obtained from it by distillation. It is a tribasic acid, and forms, like tribasic phosphoric acid (p. 232), three series of salts, having the formulæ, respectively—

$$3MO . Cy_3O_3,\ 2MO . HO . Cy_3O_3, \text{ and } MO . 2HO . Cy_3O_3.$$

* The Fe_2 contained in ferricyanogen are equivalent to H_2 or K_2, as in Fe_2Cl_3, hence the Cy_6Fe_2 requires only H_3 or K_3 to complete the saturation of the Cy_6.

The *cyanide of phosphorus*, PCy_3, has been sublimed in tabular crystals from a mixture of cyanide of silver and terchloride of phosphorus heated in a sealed tube to 280° F. for some hours, and afterwards distilled in a current of dry carbonic acid. Cyanide of phosphorus inflames at a very low temperature, and is decomposed by water, yielding cyanic and phosphorous acids.

330. *Nitroprussides.*—When ferrocyanide of potassium is boiled with dilute nitric acid, a point is attained at which the solution gives a dark-coloured precipitate with a per-salt of iron; if it be then boiled with an excess of carbonate of soda, filtered, and evaporated, it deposits ruby-red prismatic crystals of *nitroprusside of sodium* (Na_2, $Cy_5NO_2Fe_2 + 4Aq.$), from which the nitroprussides of other metals may be obtained.

The *hydronitroprussic acid* (H_2, $Cy_5NO_2Fe_2 + 2Aq.$) has also been prepared and crystallised.

The nitroprussides have been recently proved by the late Mr Hadow to be formed from the ferricyanides by the exchange of one equivalent of cyanogen for an equivalent of nitrous acid (NO_3), and the simultaneous removal of an equivalent of the metal with which the ferricyanogen was combined. Thus ferricyanide of potassium, $K_3 . Cy_6Fe_2$, becomes nitroprusside of potassium, $K_2 . Cy_5NO_2Fe_2$, when boiled with nitric acid, other products being formed at the same time by the oxidising action of the nitric acid.

Based upon this view of its constitution, a more certain and economical process for the production of nitroprusside of sodium was devised by Hadow, which consists in acting upon the ferricyanide of potassium with nitrite of soda, acetic acid, and chloride of mercury (corrosive sublimate), when the mercury removes an equivalent of cyanogen, and the chlorine an equivalent of potassium, the nitrous acid of the nitrite of soda entering into the residue of the ferricyanide, and converting it into nitroprusside of potassium, which, by double decomposition with the acetate of soda, yields acetate of potash and nitroprusside of sodium. The cyanide of mercury crystallises out first, and the nitroprusside of sodium may be obtained in crystals from the evaporated solution.

The nitroprusside of sodium is used as a test for the alkaline sulphids, with a very slight trace of which it gives a magnificent purple colour. Thus, an inch or two of human hair, fused with carbonate of soda before the blowpipe, will yield sufficient sulphide of sodium to strike a purple tint with the nitroprusside.

331. THE FULMINATES.—The violently explosive compound known as *fulminate of mercury*, which is so largely employed for the manufacture of percussion caps, is connected with the series of cyanogen compounds.

Preparation of fulminate of mercury.—This substance is prepared by the action of alcohol upon a solution of mercury in excess of nitric acid; and as this action is of a violent character, some care is necessary in order to avoid an explosion. On a small scale, the fulminate may be obtained without any risk by strictly attending to the following prescription:—

Weigh out, in a watch-glass, 25 grains of mercury, transfer it to a half-pint beaker, add half an ounce (measured) of ordinary concentrated nitric acid (sp. gr. 1·42), and apply a gentle heat. As soon as the last particle of mercury is dissolved, place the beaker upon the table, away from any flame, and pour into it, pretty quickly, at arm's length, 5 measured drachms of alcohol (sp. gr. 0·87). Very brisk action will ensue, and the solution will become turbid from the separation of crystals of the fulminate, at the same time evolving very dense white clouds, which ve an agreeable odour, due to the presence of nitrous ether, aldehyde, and ther

products of the action of nitric acid upon alcohol. The heavy character of these liquids is caused by the presence of mercury, though in what form has not been ascertained; much nitrous oxide and hydrocyanic acid are evolved at the same time. When the action has subsided, the beaker may be filled with water, the fulminate allowed to settle, and the acid liquid poured off. The fulminate is then collected on a filter, washed with water as long as the washings taste acid, and dried by exposure to air.

The chemical change involved in the preparation of the fulminate is complicated by the formation of the secondary products of the action of nitric acid upon alcohol, but if these be left out of consideration, a clear idea of the reaction may be obtained.

The fulminate of mercury is found, on analysis, to contain mercury, carbon, nitrogen, and oxygen in proportions corresponding to the formula HgC_2NO_2; if the mercury be supposed to exist in the state of oxide, into which it would have been converted by the nitric acid, this formula might be written $HgO.C_2NO$. The formula for alcohol is $C_4H_6O_2$, and if the above expression for fulminate of mercury be doubled, it becomes $2HgO.C_4N_2O_2$, and appears to be derivable from alcohol by the exchange of H_6 for N_2, and the addition of $2HgO$. It has been remarked (p. 133) that the action of nitrous acid (NO_3) upon organic substances frequently results in the removal of H_3 from the substance in the form of $3HO$; and it may be supposed that this acid, resulting from the de-oxidation of the nitric acid by one portion of the alcohol, has acted upon another portion so as to eliminate the whole of its hydrogen, and to leave, in exchange, 2 eqs. of nitrogen; thus, $C_4H_6O_2 + 2NO_3 = C_4N_2O_2 + 6HO$. It is evident that the combining value of the two atoms of triatomic nitrogen is equal to that of six atoms of hydrogen.* The substance $C_4N_2O_2$, supposed to be combined with the oxide of mercury (though never obtained in the separate state), has been named *fulminic acid*. The chemical constitution of the fulminate will be more advantageously discussed when its properties have been considered.

Properties of fulminate of mercury.—This substance is deposited in the above process in fine needle-like crystals, which often have a grey colour from the accidental presence of a little metallic mercury. It may be purified by boiling it with water, in which it is sparingly soluble, and allowing the fulminate to crystallise from the filtered solution. Very moderate friction or percussion will cause it to detonate violently, so that it must be kept in a corked bottle lest it should be exploded between the neck and the stopper. Its explosion is attended with a bright flash, and with grey fumes of metallic mercury. The simplest equation to represent the decomposition would be $Hg_2C_4N_2O_4 = Hg_2 + 4CO + N_2$; and its violence must be attributed to the sudden evolution of a large volume of gas and vapour from a small volume of solid, for the fulminate of mercury, being exceedingly heavy (sp. gr. 4·4), occupies a very small space when compared with the gaseous products of its decomposition, especially when the latter are expanded by the heat. The evolution of heat during the explosion, apparently in contradiction to the rule that heat is absorbed in decomposition, must be ascribed to the circumstance that the heat evolved by the oxidation of the carbon exceeds that absorbed in the decomposition of the fulminate. A temperature of 360° F. explodes fulminate of mercury, and the same result is brought about by touching it with a glass rod

* This view is supported by the circumstance that fulminate of silver is abundantly formed when nitrous acid is passed into an alcoholic solution of nitrate of silver.

dipped in concentrated sulphuric or nitric acid. The electric spark of course explodes it.

Cap composition.—The explosion of the fulminate of mercury is so violent and rapid that it is necessary to moderate it for percussion-caps. For this purpose it is mixed with nitrate or chlorate of potash, the oxidising property of these salts possibly causing them to be preferred to any merely inactive substances, since it would tend to increase the temperature of the flash by burning the carbonic oxide into carbonic acid, and would thus ensure the ignition of the cartridge. For military caps in this country, chlorate of potash is always mixed with the fulminate, and powdered glass is sometimes added to increase the sensibility of the mixture to explosion by percussion. Sulphide of antimony is sometimes substituted for powdered glass, apparently for the purpose of lengthening the flash by taking advantage of the powerful oxidising action of chlorate of potash upon that compound (p. 157). Since the composition is very liable to explode under friction, it is made in small quantities at a time, and without contact with any hard substance. After a little of the composition has been introduced into the cap, it is made to adhere and waterproofed by a drop of solution of shell-lac in spirit of wine.

If a thin train of fulminate of mercury be laid upon a plate, and covered, except a little at one end, with gunpowder, it will be found on touching the fulminate with a hot wire, that its explosion scatters the gunpowder, but does not inflame it. On repeating the experiment with a mixture of 10 grains of the fulminate and 15 grains of chlorate of potash, made upon paper with a card, the explosion will be found to inflame the gunpowder.

By sprinkling a thin layer of the fulminate upon a glass plate, and firing it with a hot wire, the separated mercury may be made to coat the glass, so as to give it all the appearance of a looking-glass.

Although the effect produced by the explosion of fulminate of mercury is very violent in its immediate neighbourhood, it is very slightly felt at a distance, and the sudden expansion of the gas will burst fire-arms, because it does not allow time for overcoming the inertia of the ball, though, if the barrel escape destruction, the projectile effect of the fulminate is found inferior to that of powder.

The fulminate of mercury is generally contaminated with oxalate of mercury ($HgO . C_2O_3$), which is one of the secondary products formed during its preparation.

Fulminate of silver is prepared by a process very similar to that for fulminate of mercury, but since its explosive properties are far more violent, it is not advisable to prepare so large a quantity. 10 grains of pure silver are dissolved, at a gentle heat, in 70 minims of ordinary concentrated nitric acid (sp. gr. 1·42) and 50 minims of water. As soon as the silver is dissolved, the heat is removed, and 200 minims of alcohol (sp. gr. 0·87) are added. If the action does not commence after a short time, a very gentle heat may be applied until effervescence begins, when the fulminate of silver will be deposited in minute needles, and may be further treated as in the case of fulminate of mercury.* When dry, the fulminate of silver must be handled with the greatest caution, since it is exploded far more easily than the mercury salt; it should be kept in small quantities wrapped up separately in paper, and placed in a card-board box.

* If the nitric acid and alcohol are not of the exact strength here prescribed, it may be somewhat difficult to start the action unless two or three drops of red nitric acid (containing nitrous acid) are added. Standard silver (containing copper) may be used for preparing fulminate.

Nothing harder than paper should be employed in manipulating it. The violence of its explosion renders it useless for percussion caps, but it is employed in detonating crackers. Fulminate of silver is sparingly soluble in cold water, but dissolves in 36 parts of boiling water.

If a minute particle of fulminate of silver be placed upon a piece of quartz, and gently pressed with the angle of another piece, it will explode with a flash and smart report.

A *throw-down* detonating cracker may be made by screwing up a particle of the fulminate of silver in a piece of thin paper, with some fragments obtained by crushing a common quartz pebble.

The explosion of fulminate of silver may be compared with that of the mercury salt by heating equal quantities upon thin copper or platinum foil, when the fulminate of mercury will explode with a slight puff, and will not injure the foil, but that of silver will give a loud crack and rend a hole in the metal.

If a particle of fulminate of silver be placed upon a glass plate and touched with a glass rod dipped in oil of vitriol, it will detonate and leave a deposit of silver upon the glass.

When fulminate of silver is dissolved in warm ammonia, the solution deposits, on cooling, crystals of a *double fulminate of silver and ammonia*, $AgO.NH_3.HO.C_4N_2O_2$, which is even more violently explosive, and is dangerous while still moist.

On adding chloride of potassium in excess to fulminate of silver, only half the silver is removed as chloride, and the *double fulminate of silver and potassium*, $AgO, KO, C_4N_2O_2$, may be crystallised from the solution. By the careful addition of nitric acid, the KO may be removed from this salt, and the *acid fulminate of silver*, $AgO.HO.C_4N_2O_2$, obtained, which is easily soluble in boiling water, and crystallises out on cooling; by boiling with oxide of silver, it is converted into the neutral fulminate.

Various other fulminates and double fulminates have been obtained. They are all more or less explosive.

Chemical constitution of the fulminates.—The fact of the existence of double fulminates and acid fulminates renders it necessary to write the empirical formula of fulminate of silver, for example, $Ag_2C_4N_2O_4$, instead of AgC_2NO_2, in order to show that half of the silver is capable of being exchanged for another metal or for hydrogen. It will be seen that this formula would also represent two equivalents of cyanate of silver ($AgO.C_2NO$), but the properties of this salt are entirely different from those of the fulminate. That a strong connection exists, however, between the fulminates and the cyanogen-compounds, is shown by several reactions. Thus, if fulminate of mercury be heated with hydrochloric acid, it is dissolved with evolution of a powerful odour of hydrocyanic acid, whilst mercuric chloride and oxalate, with hydrochlorate of ammonia, remain in the solution. Again, if an excess of fulminate of silver be acted on by hydrosulphuric acid, cyanic acid may be obtained in solution, and becomes converted into hydrosulphocyanic acid, when the hydrosulphuric acid is in excess. By decomposing the double fulminate of copper and ammonia ($CuO.NH_3.HO.C_4N_2O_2$) with hydrosulphuric acid, there are produced hydrosulphocyanic acid and urea, the latter having the same composition as cyanate of ammonia—

$$CuO.NH_3.HO.C_4N_2O_2 + 3HS = CuS + 2HO + \underset{\text{Hydrosulphocyanic acid.}}{H.C_2NS_2} + \underset{\text{Urea.}}{C_2H_4N_2O_2}.$$

These reactions have induced many chemists to regard the fulminates as *compounds of the metallic oxides* with an acid having the composition

Cy_2O_2, intermediate in composition between the hypothetical anhydrous cyanic acid (CyO) and the hypothetical anhydrous cyanuric acid (Cy_2O_3), but neither the anhydrous nor the hydrated fulminic acid has yet been obtained in a separate form. This view of the constitution of the fulminates, however, has the recommendation of simplicity, and enables the greater number of their reactions to be easily explained.

Fulminate of mercury dissolves when boiled with solution of chloride of potassium, and the solution, when evaporated, yields crystals of *fulminurate* or *isocyanurate* of potash, $KO.C_6N_3H_2O_5$, which has the same percentage composition as acid cyanurate of potash, $KO.2HO.Cy_3O_3$, but the acid contained in fulminurate of potash forms only one series of salts, and is therefore monobasic. The fulminurates are feebly explosive. The production of fulminuric acid from the hypothetical hydrate of fulminic acid may be represented by the equation—

$$2(2HO.C_4N_2O_2) + 2HO = 2CO_2 + NH_3 + HO.C_6N_3H_2O_5.$$

PRODUCTS OF THE DESTRUCTIVE DISTILLATION OF COAL.

332. Much of the extraordinary progress made by chemistry during the last half century must be attributed to the introduction and gradual extension of the manufacture of coal-gas. No other branch of manufacture has brought into notice so many compounds not previously obtained from any other source; and, above all, offering, at first sight, so very little promise of utility, as to press urgently upon the chemist the necessity for submitting them to investigation.

Although many important additions to chemical knowledge have resulted from the labours of those who have engaged in devising the best methods of obtaining the coal-gas itself in the state best fitted for consumption, far more benefit has accrued to the science from investigations into the nature of the secondary products of the manufacture, the removal of which was the object to be attained in the purification of the gas.

Of the compounds of carbon and hydrogen, very little was known previously to the introduction of coal-gas; and although the liquid hydrocarbons composing coal-naphtha were originally obtained from other sources, the investigation of their chemical properties has been greatly promoted by the facility with which they may be obtained in large quantities from that liquid. The most important of these hydrocarbons, *benzole* or *benzine*, was originally procured from benzoic acid; but it would have been impossible for it to have fulfilled its present useful purposes but for the circumstance that it is obtained in abundance as a secondary product in the manufacture of coal-gas; for, leaving out of consideration the various uses to which benzole itself is devoted, it yields the *nitrobenzole*, so much used in perfumery, and from this we obtain *aniline*, from which many of the most beautiful dyes are now prepared.

The *naphthaline* found so abundantly in coal-tar possesses a peculiar interest, as having formed the subject of the beautiful researches by which Laurent was led to propose the doctrine of substitution, which has since thrown so much light upon the constitution of organic substances.

We are also especially indebted to coal-tar for our acquaintance with the very interesting and rapidly-extending class of volatile alkalies, of which the above-mentioned aniline is the chief representative, and for *phenic* or *carbolic acid*, from which are derived the large number of substances composing the phenyle-series.

The retorts in which the distillation of coal is effected are made either of t-iron or stoneware, generally having the form of a flattened cylinder, and anged in sets of three or five, heated by the same coal fire (fig. 267). The arge for each retort is about two bushels, and is thrown on to the red-hot

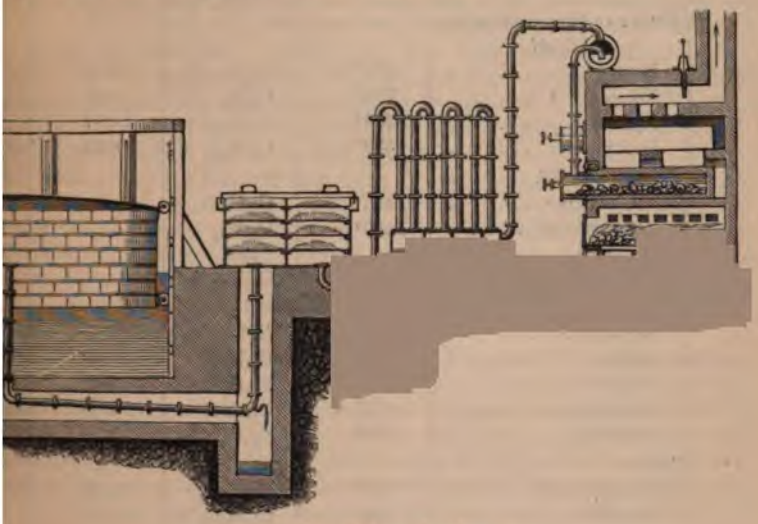


Fig. 267.—Manufacture of coal-gas.

r of the retort, as soon as the coke from the previous distillation has been ed out; the mouth of the retort is then closed with an iron plate luted h clay. An iron pipe rises from the upper side of the front of the retort jecting from the furnace, and is curved round at the upper extremity, ich passes into the side of a much wider tube, called the *hydraulic in*, running above the furnaces, at right angles to the retorts, and re- ving the tubes from all of them. This tube is always kept half full of tar and water which condense from the gas, and below the surface of s liquid the delivery tubes from the retorts are allowed to dip, so that hough the gas can bubble freely through the liquid as it issues from retort, none can return through the tube whilst the retort is open for introduction of a fresh charge.

The aqueous portion of the liquid deposited in the hydraulic main is own as the *ammoniacal liquor*, from its consisting chiefly of a solution various salts of ammonia, the chief of which is the sesquicarbonate; phide, cyanide, and sulphocyanide of ammonium are also found in it.

From the hydraulic main the gas passes into the *condenser*, which is mposed of a series of bent iron tubes kept cool either by the large sur- e which they expose to the air, or sometimes by a stream of cold er. In these are deposited, in addition to water, any of the volatile drocarbons and salts of ammonia which may have escaped condensation the hydraulic main. Even in the condenser the removal of the am- niacal salts is not complete, so that it is usually necessary to pass the through a *scrubber* or case containing fragments of coke, over which a eam of water is allowed to trickle in order to absorb the remaining moniacal vapours.

The *tar* which condenses in the hydraulic main is a very complex mixture, of which the following are some of the leading components—

	Boiling Point.	Equivalent Formula.	Sp. Gr.
NEUTRAL HYDROCARBONS.			
Liquid.			
Benzole, ...	176° F.	$C_{12}H_6$	0·88
Toluole, ...	230°	$C_{14}H_8$	0·87
Xylole, ...	284°	$C_{16}H_{10}$	0·87
Isocumole*	338°	$C_{18}H_{12}$	0·85
Solid.			
Naphthaline, ...	428°	$C_{20}H_8$	
Paranaphthaline, . .	580°	$C_{20}H_{12}$	
Chrysene, ...	...	$C_{24}H_8$	
Pyrene, ...	...	$C_{30}H_{12}$	
ALKALINE PRODUCTS.			
Ammonia, ...	...	NH_3	
Aniline, ...	360°	$C_{12}H_7N$	1·02
Picoline, ...	271°	$C_{12}H_7N$	0·96
Quinoline, ...	462°	$C_{18}H_7N$	1·08
Pyridine, ...	240°	$C_{10}H_5N$	
ACIDS.			
Carbolic acid, . . .	370°	$C_{12}H_6O_2$	1·07
Kresylic „	397°	$C_{14}H_8O_2$	
Rosolic „	...	$C_{44}H_{28}O_6$	
Brunolic „			
Acetic „	243°	$C_4H_4O_4$	1·06

The gas is now passed through the *lime-purifier*, which is an iron b with shelves, on which dry slaked lime is placed in order to absorb t carbonic acid and sulphuretted hydrogen, and the last portions of ammo are removed by passing the gas through dilute sulphuric acid.

A great many other methods have been devised for the purification the gas from sulphuretted hydrogen, but none appears to be so efficaci and economical as that which consists in passing the gas over a mixt of sulphate of iron (green vitriol or copperas), slaked lime, and sawd (which is employed to prevent the other materials from caking togeth The lime decomposes the sulphate of iron, forming sulphate of lime hydrated oxide of iron—

$$FeO.SO_3 + CaO.HO = FeO.HO + CaO.SO_3.$$

The action of air upon the mixture soon converts the oxide into ses oxide of iron, which absorbs the sulphuretted hydrogen and the hy cyanic acid, producing with the former sulphide of iron, and with latter Prussian blue, or some similar compound. The sulphate of l existing in this purifying mixture is useful in absorbing any vapou carbonate of ammonia from the gas, forming sulphate of ammonia carbonate of lime.†

* *Benzole*, originally derived from *benzoic acid*; *toluole*, from balsam of *tolu*; *xy* found among the products from *wood* (ξύλον); isocumole, isomeric with cumole, obta from oil of *cummin*.

† Sesquioxide of iron itself, derived from various natural and artificial sources, is employed for the purification of coal-gas.

The action of the sulphuretted hydrogen on the sesquioxide of iron may be thus represented, $Fe_2O_3 + 3HS = 2FeS + S + 3HO$; and the circumstance which especially conduces to the economy of the process, is the facility with which the sulphide of iron may be reconverted into the sesquioxide by mere exposure to the action of atmospheric oxygen, for $2FeS + O_3 = Fe_2O_3 + S_2$, thus reviving the power of the mixture to absorb sulphuretted hydrogen. Accordingly, if a small quantity of air be admitted into the purifier together with the gas, it reconverts the sulphide of iron into sesquioxide, and the oxidation is attended with enough heat to convert into vapour any benzole which may have condensed in the purifying mixture, and of which the illuminating value would otherwise be lost. The same purifying mixture may thus be employed to purify a very large quantity of gas, until the separated sulphur has increased its bulk to an inconvenient extent, when it is distilled off in iron retorts. The various processes which have been devised for the removal of the bisulphide of carbon vapour are mentioned at p. 217.

The purified gas is passed into the gasometers, from which it is supplied for consumption.

In the manufacture of coal-gas, attention is requisite to the temperature at which the distillation is effected, for if it be too low, the solid and liquid hydrocarbons will be formed in too great abundance, not only diminishing the volume of the gas, but causing much inconvenience by obstructing the pipes. On the other hand, if the retort be too strongly heated, the vapours of volatile hydrocarbons, as well as the olefiant gas and marsh-gas, may undergo decomposition, depositing their carbon upon the sides of the retort, in the form of gas-carbon, and leaving their hydrogen to increase the volume and dilute the illuminating power of the gas.

These effects are well exemplified in the following analyses of the gas collected from Wigan cannel coal at different periods of the distillation:—

In 100 volumes.	1st hour.	5th hour.	10th hour.
Olefiant gas and volatile hydrocarbons,	13·0	7·0	0·0
Marsh-gas, ...	82·5	56·0	20·0
Carbonic oxide, ...	3·2	11·0	10·0
Hydrogen, ...	0·0	21·3	60·0
Nitrogen, ...	1·3	4·7	10·0

The increase of the carbonic oxide after the first hour must be attributed to the decomposition of the aqueous vapour by the carbon as the temperature rises, and the increase of the nitrogen may probably be ascribed to the decomposition of the ammonia into its elements at a high temperature.

333. One of the most useful of the secondary products of the coal-gas manufacture is the ammonia, and this process has been already noticed as a principal source of the ammoniacal salts found in commerce.

Next in the order of usefulness stands the coal-tar, which deserves attentive consideration not only on that account, but because the extraction of the various useful substances from this complex mixture affords an excellent example of *proximate organic analysis*, that is, of the separation of an organic mixture into its immediate components.

For the separation of the numerous volatile substances contained in

coal-tar, advantage is taken of the difference in their boiling points, which will be observed on examining the table at p. 450.

A large quantity of the tar is distilled in an iron retort, when water passes over, holding salts of ammonia in solution, and accompanied by a brown oily offensive liquid which collects upon the surface of the water. This is a mixture of the hydrocarbons which are lighter than water, viz., benzole, toluole, xylole, and isocumole, all having, as represented in the table at p. 450, a specific gravity of about 0·85. 100 parts of the tar yield, at most, 10 parts of this *light oil*.

As the distillation proceeds, and the temperature rises, a yellow oil distils over, which is heavier than water, and sinks in the receiver. This oil, commonly called *dead oil*, is much more abundant than the light oil, amounting to about one-fourth of the weight of the tar, and contains those constituents of the tar which have a high specific gravity and boiling point, particularly naphthaline, aniline, quinoline, and carbolic acid. The proportion of naphthaline in this oil augments with the progress of the distillation, as would be expected from its high boiling point, so that the last portions of the oil which distil over become nearly solid on cooling. When this is the case, the distillation is generally stopped, and a black viscous residue is found in the retort, which constitutes *pitch*, and is employed for the preparation of Brunswick black and of asphalt for paving.

The light oil which first passed over is rectified by a second distillation, and is then sent into commerce under the name of *coal naphtha*, a quantity of the heavy oil being left in the retort, the lighter oils having lower boiling points.

This coal naphtha may be further purified by shaking it with sulphuric acid, which removes several of the impurities, whilst the pure naphtha collects on the surface when the mixture is allowed to stand. When this is again distilled it yields the *rectified coal naphtha*.

This light oil, especially when distilled from cannel coal at a low temperature, contains, in addition to the hydrocarbons above enumerated, some belonging to the marsh-gas series (C_nH_{2n}), and others more recently brought to light, belonging to a series the general formula of which is C_nH_{n-2}; but these last appear to be acted on by the sulphuric acid, employed to remove the basic substances from the light oil, in such a manner that they are converted into polymeric hydrocarbons, having the general formula $C_{2n}H_{2n-4}$, of which the three following have been particularly examined:—

Equivalent formula.	Boiling point.
$C_{24}H_{20}$	410° F.
$C_{28}H_{24}$	464°
$C_{32}H_{28}$	536°

The hydrocarbons, $C_{12}H_{10}$, $C_{14}H_{12}$, and $C_{16}H_{14}$, from which these appear to have been formed by the action of sulphuric acid, would evidently be the higher homologues of acetylene, C_4H_2.

The distillation of cannel coal, and of various minerals nearly allied to coal, at low temperatures, is now extensively carried on for the manufacture of paraffine and paraffine oil. (*See Paraffine.*)

The separation of the hydrocarbons composing this naphtha is effected by a process in constant use for similar purposes, and known as *fractional distillation*.

This consists in distilling the liquid in a retort (A, fig. 268) through the tubulure of which a thermometer (T) passes, to indicate the temperature at which it boils. The first portion which distils over will, of course,

consist chiefly of that liquid which has the lowest boiling point; and if the receiver (R) be changed at stated intervals corresponding to a certain

Fig. 268.—Fractional distillation.

rise in the temperature, a series of liquids will be obtained, containing substances the boiling points of which lie within the limits of temperature between which such liquids were collected.

When these liquids are again distilled separately in the same way, a great part of each is generally found to distil over within a few degrees on either side of some particular temperature, which represents the boiling point of the substance of which that liquid chiefly consists; and if the receivers be again changed at stated intervals, a second series of distillates will be obtained, the boiling points of which are comprised within a narrower range of temperature. It will be evident that, by repeated distillations of this description, the mixture will eventually be resolved into a number of substances, each distilling over entirely at or about one particular degree, viz., the boiling point of that substance.

To apply this to the separation of the constituents of light coal naphtha.

The crude light oil is first agitated with dilute sulphuric acid, which removes any basic substances present in it, and afterwards with a dilute solution of potash, to separate carbolic acid. The adhering potash is removed by shaking with water, and the naphtha is allowed to remain at rest, so that all the water may settle down, and the naphtha may be drawn off for distillation.

The naphtha begins to boil at about 160° F., but a small quantity distils over before the temperature has risen to 180°, when the receiver may be changed; between 180° and 200° a considerable quantity of the naphtha distils over, and at the latter degree the receiver is changed a second time. The receiver is changed at every 20° throughout the distillation, until nearly the whole of the naphtha has passed over, which will be the case at about 360°.*

Ten unequal quantities of liquid will have been thus obtained, diminishing as the temperature rises.

Each of these must then be distilled in a smaller retort than the first, also provided with a thermometer.

The first portion (160° to 180°) will probably begin to boil at 150°, and will distil in great part before 160°, when the receiver may be changed. When the temperature reaches 170° it will probably be found that nothing remains worth distilling. The liquid passing over in this distillation between 160° and 170° may be added to that which is next to be distilled (180° to 200°).

* On the large scale, that portion of the naphtha which is distilled over between 180° and 250° F. *is sold as benzole, and employed* for the preparation of aniline.

The second portion (180° to 200°) will begin to boil at about 175°, and will distil over chiefly between that temperature and 185°, when the receiver may be changed. Nearly the whole will have passed over before 195°, and this last fraction may be added to that previously obtained from 200° to 220°.

When all the first series of liquids have been thus distilled, it will be found that the second series consists chiefly of six portions distilling between the following degrees of temperature, viz., 150°–160°, 175°–185°, 180°–190°, 240°–250°, 300°–310°, 340°–350°.

By another distillation of each of these portions, a third series of liquids will be formed, consisting chiefly of five portions distilling between the following points, viz. 145°–150°, 175°–180°, 230°–235°, 288°–293°, 336°–342°.

The portion distilling between 145° and 150° is comparatively small in quantity, and has not yet been fully examined.

That obtained between 175° and 180° is more abundant than either of the others, and is nearly pure benzole ($C_{12}H_6$).

The portion boiling between 230° and 235° is chiefly toluole ($C_{14}H_8$), whilst 288° to 293° gives xylole ($C_{16}H_{10}$), and 336° to 342° isocumole ($C_{18}H_{12}$).

In order to separate the benzole completely from the hydrocarbons which still adhere to it, the portion boiling between 175° and 180° is exposed to a temperature of 32°, when the benzole alone freezes, the other hydrocarbons remaining liquid, and being easily extracted by pressure.

A simpler method of separating liquids which have different boiling points consists in distilling them in a flask (F, fig. 269) connected with a spiral worm (W) of

Fig. 269.—Fractional distillation.

pewter or copper, surrounded by water, or some other liquid, maintained at a temperature just above the boiling point of the particular liquid which is required to distil over. The greater part of the less volatile liquids will condense in the worm and run back into the flask. Thus, in extracting benzole from the light oil, the liquid in A might be kept at 180° F., when the toluole, &c., would be partly condensed in the worm, and the portion which passed into the receiver would consist chiefly of benzole. When little more distilled over, the temperature of A might be raised to 230° and the receiver changed, when the distillate would contain toluole as its predominant constituent, and so on.

334. *Benzole.*—The pure benzole or benzine is a brilliant colourless liquid, exhaling a powerful odour of coal-gas; it boils at 176° F., and is very inflammable, burning with a smoky flame. It mixes readily with alcohol and wood-spirit, but not with water. Its property of dissolving caoutchouc and gutta percha renders it very useful in the arts, and it is an excellent solvent for the removal of grease, paint, &c., from clothes and furniture.

nzole combines directly with chlorine to form a solid *chloride of benzole*, $C_{12}H_6Cl_6$, is decomposed by an alcoholic solution of potash, yielding *chlorobenzole*, Cl_3.

the action of an aqueous solution of hypochlorous acid upon benzole, a crys- e body has been obtained, having the composition $C_{12}H_9Cl_3O_6$, and called *orhydrine of phenose*. When acted on by alkalies, this substance yields a sweet ance called *phenose*, isomeric with dry grape-sugar—

$$C_{12}H_9Cl_3O_6 + 3(KO.HO) = \underset{\text{Phenose.}}{C_{12}H_{12}O_{12}} + 3KCl.$$

ils substance has not been crystallised; it forms a deliquescent amorphous which is easily soluble in water and alcohol, but insoluble in ether. It reduces xides of copper and silver like grape-sugar, and when acted on by nitric acid verted into oxalic acid. Phenose has not been found capable of fermentation ast.

5. *Aniline.*—The chief purpose to which benzole is devoted is the ration of aniline, which is subsequently converted into the bril- dyes now so extensively used. It has been already noticed at 8, that when benzole is dissolved in fuming nitric acid, violent action place, and a dark red liquid is formed, from which water precipitates avy yellow oily liquid, smelling of bitter almonds, and known as *benzole*, which has the composition $C_{12}H_5(NO_4)$, and may be regarded rived from benzole by the substitution of an equivalent of nitric per- for an equivalent of hydrogen—

$$\underset{\text{Benzole.}}{C_{12}H_6} + HO.NO_5 = \underset{\text{Nitrobenzole.}}{C_{12}H_5(NO_4)} + 2HO.$$

n nitrobenzole is placed in contact with diluted sulphuric acid and llic zinc, the (nascent) hydrogen removes the whole of the oxygen, wo equivalents of hydrogen are acquired in their stead, producing NH_2, or $C_{12}H_7N$, *aniline*—

$$\underset{\text{Nitrobenzole.}}{C_{12}H_5(NO_4)} + H_6 = \underset{\text{Aniline.}}{C_{12}H_7N} + 4HO.*$$

aniline has been produced may be shown by neutralising the excess phuric acid with potash, and adding chloride of lime (hypochlorite ne), which gives a fine purple colour with aniline.

e conversion of nitrobenzole into aniline on a large scale is more niently effected by gently heating it in a retort, with water, iron s, and acetic acid, when the deoxidising action of the acetate of iron $C_4H_3O_3$), first produced, materially assists the change, this salt converted into a basic peracetate of iron ($Fe_2O_3.2C_4H_3O_3$), which is n the retort, and the aniline may be distilled over, accompanied by . At the close of the distillation, a red oil passes over, which solidi- o a crystalline mass. This is *azobenzide*, $C_{12}H_5N$, originally obtained stilling nitrobenzole with an alcoholic solution of potash.

Then nitrobenzole, in alcoholic solution, is reduced by zinc in the nce of hydrochloric acid, the solution neutralised by carbon ate of

he change is more intelligible when molecular formulæ are employed; thus—

	Molecular formula.
Benzole, . .	Θ_6H_6
Nitrobenzole, .	$\Theta_6H_5(N\Theta_2)$
Aniline, . .	$\Theta_6H_5NH_2$

shows that two *atoms* of oxygen have been displaced by two atoms of hydrogen.

soda and boiled with alcohol, a crystalline compound of aniline with chloride of zinc ($ZnCl + C_{12}H_7N$) is obtained.)

Since aniline is only slightly soluble in water, and has the sp. gr. 1·02, the larger portion of it collects at the bottom of the liquid in the receiver, which is milky from the presence of minute drops of aniline in suspension. By pouring the contents of the receiver into a tall vessel, the greater part of the aqueous fluid may be separated, and the aniline may be purified by a second distillation, when the remaining water will pass over first, the boiling point of aniline being 360° F.

Aniline* presents many striking features; though colourless when perfectly pure, it soon becomes brown if exposed to the air; its odour is very peculiar and somewhat ammoniacal, and its taste is very acrid. A drop falling upon a deal table stains it intensely yellow. But the character by which aniline is most easily recognised, and that which leads to its useful applications, is the production of a violet colour with solution of chloride of lime, by which a very minute quantity of aniline may be detected. The exact nature of the chemical change connected with the production of this colour has not been determined, but it is known to be an oxidation, and a great number of processes have been patented from time to time for the production of crimson, purple, and violet dyes by the action of various oxidising agents upon aniline.

336. *Coal-tar dyes.*—The first dye ever manufactured from aniline on a large scale was that known as *mauve*,† or *aniline purple*, which is obtained by dissolving aniline in diluted sulphuric acid, and adding solution of bichromate of potash, when the liquid gradually becomes dark-coloured, and deposits a black precipitate, which is filtered off, washed, boiled with coal-naphtha to extract a brown substance, and afterwards treated with hot alcohol, which dissolves the mauve. The chemical change by which the aniline has been converted into this colouring-matter cannot at present be clearly traced, but the basis of the colour has been found to be a substance which has the composition $C_{27}H_{12}N_2$, and has been termed *mauvéine*. It forms black shining crystals, resembling specular iron ore, which dissolve in alcohol, forming a violet solution, and in acids, with production of the purple colour. Mauvéine combines with the acids to form salts; its alcoholic solution even absorbs carbonic acid gas. The *hydrochlorate of mauvéine*, $C_{27}H_{12}N_2 . HCl$, forms prismatic needles with a green metallic lustre.

Very brilliant red dyes are obtained from commercial aniline by the action of bichloride (tetrachloride) of carbon, bichloride of tin, perchloride of iron, chloride of copper, mercuric nitrate, corrosive sublimate, and hydrated arsenic acid. It will be noticed that all these agents are capable of undergoing reduction to a lower state of oxidation or chlorination, indicating that the chemical change concerned in the transformation of aniline into aniline-red is one in which the aniline is acted on by oxygen or chlorine.

The easiest method of illustrating the production of aniline-red, on the small scale, consists in heating a few drops of aniline in a test-tube with a fragment of corrosive sublimate (perchloride of mercury), which soon fuses and acts upon the aniline to form an intensely red mass composed of aniline-red, calomel, and various secondary products. By heating this mixture with alcohol the red dye is dissolved, and a skein of silk or wool dipped into the liquid becomes dyed of a fine red, which is not removed by washing.

On the large scale, *Magenta* (as aniline-red is commonly termed) is generally prepared by heating aniline to about 320° F. with hydrated arsenic acid, when a dark semisolid mass is obtained, which becomes hard and brittle on cooling, and exhibits a green metallic reflection. This mass contains, in addition to aniline-red, several secondary products of the action, and arsenious acid. On boiling it with water, a splendid red solution is obtained, and a dark resinous or pitchy mass is left. If

* Aniline derives its name from *anil*, the Portuguese for indigo, from which it may be obtained by distillation with potash.

† French for marsh-mallow, in allusion to the colour of the flower.

mon salt be added to the red solution as long as it is dissolved, the bulk of the louring matter is precipitated as a resinous mass, which may be purified from tain adhering matters by drying and boiling with coal naphtha. The red colour- matter is a combination of arsenic acid with a *colourless* organic base, which has en called *rosaniline*, and has the composition $C_{40}H_{19}N_3 . 2HO$ (*atomic formula*, $H_{19}N_3 . H_2O$). If the red solution of arseniate of rosaniline be decomposed with drate of lime suspended in water, a pinkish precipitate is obtained, which consists rosaniline mixed with arseniate of lime, and the solution entirely loses its red lour.

By treating the precipitate with a small quantity of acetic acid, the rosaniline is nverted into *acetate of rosaniline* ($C_{40}H_{19}N_3$, $HO . C_4H_3O_3$), forming a red solution, hich may be filtered off from the undissolved arseniate of lime. On evaporating e solution to a small bulk, and allowing it to stand, the acetate is obtained in ystals which exhibit the peculiar green metallic lustre of the wing of the rose- etle, characteristic of the salts of rosaniline. This salt is the commonest com- ercial form of Magenta; its colouring power is extraordinary, a very minute particle parting a red tint to a large volume of water. Silk and wool easily extract the hole of the colouring matter from the aqueous solution, becoming dyed a fast and rilliant crimson; cotton and linen, however, have not so strong an attraction for it, o that if a pattern be worked in silk upon a piece of cambric, which is then im- ersed in a solution of Magenta and afterwards washed in hot water, the colour ill be washed out of the cambric, but the red silk pattern will be left.

If a boiling solution of the acetate of rosaniline be mixed with excess of ammonia, he bulk of the rosaniline will be precipitated, but if the solution be filtered while ot, it deposits colourless needles of rosaniline, which become red when exposed to he air, from absorption of carbonic acid, and formation of the red carbonate of osaniline.

Water dissolves but little rosaniline; alcohol dissolves it abundantly, forming a deep red solution. Rosaniline forms two classes of salts with acids, those with one equivalent of acid (*monacid* salts) being crimson, and those with three equivalents (*triacid* salts) having a brown colour. Thus, if colourless rosaniline be dissolved in a little dilute hydrochloric acid, a red solution is obtained, which contains the monacid hydrochlorate of rosaniline, $C_{40}N_{19}H_3 . HCl$; but if an excess of hydro- chloric acid be added, the red colour disappears, and a brown solution is obtained, from which the triacid hydrochlorate, $C_{40}H_{19}N_3 . 3HCl$, may be crystallised in brown- red needles.

For experimental illustration of the properties of rosaniline, the liquid obtained by boiling a solution of the acetate with a slight excess of lime diffused in water, and filtering while hot, is very well adapted. This solution has a yellow colour, and may be preserved in a stoppered bottle without alteration. If air be breathed into it through a tube, the liquid becomes red from production of carbonate of rosaniline. Characters painted on paper with a brush dipped in the solution are invisible at first, but gradually acquire a beautiful rose colour.

When the red solution of hydrochlorate of rosaniline is slightly acidified with hydrochloric acid and placed in contact with zinc, the solution becomes colourless, the rosaniline acquiring two equivalents of hydrogen, and becoming *leucaniline* (from λευκός, *white*) $C_{40}H_{21}N_3$, the hydrochlorate of which ($C_{40}H_{21}N_3 . 3HCl$) forms a colourless solution. Oxidising agents reconvert the leucaniline into rosaniline. It has been observed that *pure* aniline does not yield aniline-red when heated with corrosive sublimate or arsenic acid, it being necessary that it should contain another organic base, *toluidine* ($C_{14}H_9N$), which is derived from toluole ($C_{14}H_8$) in the same way in which aniline is derived from benzole. Since the benzole obtained from coal naphtha almost invariably contains toluole, the aniline obtained from it is very seldom free from toluidine. What share the toluidine has in the production of the red colour is not understood, but if the aniline be prepared with benzole derived from benzoic acid, and therefore free from toluole, no red is obtained. A mixture of 70 parts of toluidine with 30 of aniline, is said to answer best for the preparation of the red and violet colouring matters. Such a mixture would contain two equivalents of toluidine ($C_{14}H_9N$) and one equivalent of aniline ($C_{12}H_7N$), or $C_{40}H_{25}N_3$, only requiring the removal of H_6 by an oxidising agent to yield rosaniline $C_{40}H_{19}N_3$.

Aniline-yellow or *chrysaniline* (from χρύσεος, golden) is found among the secondary products obtained in the preparation of aniline-red. It forms a bright yellow powder resembling chrome-yellow, and having the composition $C_{40}H_{17}N_3$. It is *nearly insoluble in water, but dissolves* in alcohol. Chrysaniline has basic pro-

perties, and dissolves in acids, forming salts. On dissolving it in dilute chloric acid, and mixing the solution with the concentrated acid, a scarlet cr precipitate of *hydrochlorate of chrysaniline* ($C_{40}H_{17}N_3 . 2HCl$) is obtained, insoluble in strong hydrochloric acid, but very soluble in water. A char feature of chrysaniline is the sparing solubility of its nitrate. Even from solution of the hydrochlorate, nitric acid precipitates the nitrate of chr ($C_{40}H_{17}N_3 . HO . NO_5$) in ruby-red needles.

Aniline-blue is produced when a salt of rosaniline (the commercial sa example) is boiled with an excess of aniline, which converts the r ($C_{40}H_{19}N_3$) into *triphenylic rosaniline* ($C_{40}H_{16}(C_{12}H_5)_3N_3$), which may be re having been formed by the introduction of three equivalents of the hy radical *phenyle* ($C_{12}H_5$) in place of three equivalents of hydrogen, the lat been evolved in the form of ammonia—

$$\underset{\text{Hydrochlorate of rosaniline.}}{C_{40}H_{19}N_3 . HCl} + 3\underset{\text{Aniline.}}{[(C_{12}H_5)\,H_2N]} = \underset{\text{Hydrochlorate of triphenylic rosaniline.}}{C_{40}H_{16}\,(C_{12}H_5)_3N_3 . HCl} + 3$$

The hydrochlorate is an ordinary commercial form of aniline-blue; it ha colour, refuses to dissolve in water, but yields a fine blue solution in alco be dissolved in an alcoholic solution of ammonia, the addition of water caus precipitate of the hydrated base, triphenylic rosaniline, $C_{40}H_{16}(C_{12}H_5)_3$ which becomes bluish when washed and dried.

Just as rosaniline yields leucaniline when acted on with nascent hy triphenylic rosaniline yields triphenylic leucaniline ($C_{40}H_{18}(C_{12}H_5)_3N_3$); basic like leucaniline, but a colourless neutral substance, which is recon blue by oxidising agents. Compounds corresponding to triphenylic rosan containing methyle, ethyle, or amyle in place of phenyle, are obtained by rosaniline with the iodides of these radicals, at a high temperature, in sea Thus, by the action of iodide of ethyle (C_4H_5I) upon rosaniline, a blue body, insoluble in water but soluble in alcohol, is obtained, which is a com ethyle with triethylic rosaniline; $C_{40}H_{16}(C_4H_5)_3N_3$.

$$\underset{\text{Rosaniline.}}{C_{40}H_{19}N_3} + 4C_4H_5I = C_{40}H_{16}(C_4H_5)_3N_3 . \underset{\text{Ethyl-iodate of tri-ethyl-rosaniline.}}{C_4H_5I} + 3HI .$$

Aniline-violet appears to be formed in a similar manner. Other compo been obtained from aniline, presenting almost every variety of colour. A is prepared by the action of a mixture of hydrochloric acid and chlorate upon aniline, and under particular conditions a *black* may be obtained with agents. Another green has been made by acting upon Magenta with alc

When a solution of acetate of rosaniline is treated with cyanide of pot gradually loses its red colour, and deposits a white crystalline precipitat which has been termed *hydrocyan-rosaniline*, having the formula $C_{42}H_{20}N$ tains the elements of rosaniline and hydrocyanic acid; but this acid detected in it by the ordinary tests, leading to the belief that the new b be regarded as leucaniline ($C_{40}H_{21}N_3$), in which one equivalent of hydr placed by an equivalent of cyanogen ($C_{40}H_{20}(C_2N)N_3$). The hydrocyan is almost insoluble in water, and sparingly soluble in boiling alcoho precipitated from its salts by adding an alkali, it becomes pink on expos shine.

The present extensive application of aniline to the manufactur dyes affords a most striking example of the direct utility of pure to the arts, for only ten or a dozen years ago, the name of this was not known to any but scientific chemists, whilst at pres tons are annually consumed to supply the wants of the dyers of woollen goods.

337. Aniline ranks as a powerful organic base, combining rea acids to form salts which are, generally speaking, easily crystallise ammonia, it unites directly with the hydrated acids, without any s of water; thus, the formula for sulphate of aniline is $C_{12}H_7N . H$

e that for sulphate of ammonia is $NH_3 . HO . SO_3$. With the gen acids, also, aniline unites like ammonia, for hydrochlorate of e is $C_{12}H_7N . HCl$, and hydrochlorate of ammonia, $NH_3 . HCl$; xactly as the addition of potash to the salts of ammonia causes the tion of ammoniacal gas, so when added to the salts of aniline, it oitates that base in the form of oily drops, which render the liquid . This resemblance in disposition between aniline and ammonia to the impression that they must be moulded after a common type, accordingly, aniline is often represented as formed from ammonia by the substitution of the compound radical phenyle ($C_{12}H_5$) for an alent of hydrogen, and, upon this supposition, is termed *phenylamine*, $(C_{12}H_5) = C_{12}H_7N$.

his view of the constitution of aniline is supported by the circumstance formation when phenic or carbolic acid is heated with ammonia in be hermetically sealed; for there is reason to believe that this acid, tioned above as one of the chief acid products of the destructive llation of coal, is a hydrated oxide of phenyle $(C_{12}H_5)O . HO$, and action upon ammonia would then be clearly explained by the tion—

$$\underset{\text{Phenic acid.}}{(C_{12}H_5)O . HO} + NH_3 = 2HO + \underset{\substack{\text{Aniline or}\\ \text{phenylamine.}}}{NH_2(C_{12}H_5)}$$

en aniline is dissolved in alcohol and acted on by nitrous acid, two equivalents ose three equivalents of (monatomic) hydrogen, and acquire, in their stead, one alent of (triatomic) nitrogen, depositing a yellow compound, which has been *diazoamidobenzole*—

$$\underset{\text{Aniline.}}{2C_{12}H_7N} + NO_3 = \underset{\text{Diazoamidobenzole.}}{C_{24}H_{11}N_3} + 3HO .$$

en the nitrous acid acts upon a hot solution, a base is formed isomeric the above, and called *amido-diphenylimide*, which is identical with a yellow ing matter obtained by the action of stannate of soda upon a salt of aniline. Its ly acid solutions impart an intensely yellow colour to silk or wool, which is ed by heat, the base being volatile. The action of nitrous acid on aniline s an example of a general method of producing compounds in which nitrogen stituted for hydrogen.

companying the aniline in coal tar, there are found three other bases, *pyridine*, *picoline*, and *quinoline*. It will be seen that picoline $_7N$) is isomeric with aniline, from which, however, it differs in a very ing manner, for its salts are by no means easily crystallisable, and it shes no violet colour with oxidising agents, such as chloride of lime. ine occurs among the products of the distillation of bones. Quino- is also formed when some of the vegetable alkaloids are distilled hydrate of potash.

8. The other constituents of the light coal naphtha, viz., toluole, e, and isocumole, though not so important as benzole, on account of practical applications, stand in a highly interesting relation to it and ch other.

ese four liquids are members of a *homologous series*, that is, of a series *members of which differ by the same number of equivalents of the elements*. Thus, toluole ($C_{14}H_8$) is seen to contain C_2H_2 more than ole ($C_{12}H_6$), just as isocumole ($C_{18}H_{12}$) contains C_2H_2 more than xylole $_{10}$). On reference to the table at p. 450, it will be seen that the *ng points of the members* of this series are raised 54° F. for each

addition of C_2H_2. Thus, xylole ($C_{10}H_{10}$) boils at 284°, or 54° high
toluole ($C_{14}H_8$), which boils at 230°, whilst benzole ($C_{12}H_6$) boils
below this, or 176°.

The members of this group are also intimately connected with t
another homologous series, known as the *aromatic acids*, including

Benzoic acid, .	. $C_{14}H_6O_4$
Toluic acid, .	. $C_{16}H_8O_4$
Cuminic acid, .	. $C_{20}H_{12}O_4$.

By distilling each of these acids with hydrate of baryta, the cor
ing hydrocarbon is obtained, two equivalents of carbonic aci
removed by the baryta; thus,

$$\underset{\text{Benzoic acid.}}{C_{14}H_6O_4} - 2CO_2 = \underset{\text{Benzole.}}{C_{12}H_6}.$$

The similarity between this decomposition and that by whic
gas (C_2H_2) is derived from acetic acid ($C_4H_4O_4$) will be at once
(*see* p. 88).

Each member of this series of hydrocarbons, when acted upon
acid, yields a nitro-compound corresponding in composition
benzole, and this, under the influence of reducing agents (such a
of iron, or the hydrosulphate of an alkaline sulphide) yields a ba
logous with aniline.

Thus we have the three following homologous series:—

Hydrocarbon.	Nitro-compound.	Base.
Benzole, $C_{12}H_6$*	Nitrobenzole, $C_{12}H_5NO_4$	Aniline, C_{12}
Toluole, $C_{14}H_8$	Nitrotoluole, $C_{14}H_7NO_4$	Toluidine, C_{14}
Xylole, $C_{16}H_{10}$	Nitroxylole, $C_{16}H_9NO_4$	Xylidine, C_{16}

339. *Carbolic* or *phenic acid*, or *phenole* ($C_{12}H_6O_2$), derives its
chiefly from its constituting a great part of the ordinary con
kreasote (from κρέας, *flesh*, and σώζω, *to preserve*). It is also pr
cow's urine, and in that of some other animals. It is found c
the heavy or dead oil of coal tar (p. 452), particularly in that
which distils over between 300° and 400° F., when the oil is subm
fractional distillation, and it appears to be the carbolic acid which
upon this heavy oil its valuable antiseptic properties, leading to
ployment for the preservation of wood from decay.

In order to extract the acid from that portion of the dead oil which d
tween 300° and 400° F., it is shaken with a hot concentrated solution of h
potash and some solid hydrate of potash. A white crystalline mass is d
which is separated from the liquid portion and treated with a little wate
solution of carbolate of potash is obtained. This is separated from a qu
oil which floats above it, and decomposed with hydrochloric acid, when th
acid separates as an oily layer upon the surface. This is drawn off, dige
a little fused chloride of calcium to remove the water, and distilled. The
liquid, when exposed to a low temperature, solidifies to a mass of long
needles, which are liquefied even by the warmth of the hand (93° F.)

Carbolic acid has the peculiar taste and smell of kreasote. It
sparingly in water, but readily in alcohol. When a piece of deal i

* An equivalent of each of these hydrocarbons, in the state of vapour, occup
that is, four times the volume occupied by an equivalent of oxygen at the sam
ture and pressure.

olution of carbolic acid, and afterwards with hydrochloric acid, it es blue on drying.

genuineness of a commercial sample of carbolic acid may be tested by shak- out a drachm of it with half a pint of warm water, which will dissolve the acid entirely, but will leave any "dead oil" undissolved. A solution of one f caustic soda in ten parts of water should dissolve five parts of pure carbolic

en carbolic acid is shaken with one-fourth of its weight of water, and exposed temperature of 39° F., it deposits six-sided prismatic crystals of a hydrate, $_{12}O_2$. HO, which is soluble in water, alcohol, and ether, and fuses at 61° F.
e acid properties of carbolic acid are of a very feeble and doubtful character. more properly regarded as *phenylic alcohol* or hydrated oxide of phenyle, $_5O$. HO.

arbolic acid is very largely used as an antiseptic agent. In medicine found very valuable, especially for the treatment of putrid sores; in admixture with sulphite of lime, it forms the substance known as *Dougall's disinfectant.*

440. *Carbazotic acid.*—When carbolic acid is boiled with fuming nitric d, the solution, on cooling, deposits beautiful yellow crystals of *carba- ic* or *picric acid*, also called *trinitrophenic* or *nitrophenisic acid*, be- se it appears to be formed from phenic acid by the substitution of NO_4 for H_2, just as nitrobenzole is formed from benzole by the substitu- n of NO_4 for H.

The composition of picric acid, upon this view, would be expressed by e formula $HO . C_{12}H_2(NO_4)_3O$, the equivalent of water being capable of placement by a base, forming a picrate or carbazotate; thus if the acid be ded to a solution of potash, a yellow precipitate of carbazotate of potash, $KO . C_{12}H_2(NO_4)_3O$, is obtained, which has led to the employment of this d as a test for potash.

Carbazotic acid is not easily soluble in water, but dissolves readily in hol. Its solutions have the property of staining the skin and other nic matters yellow, which is turned to advantage by the silk-dyer. intensely bitter taste of the acid has also led to its employment for adulteration of beer, to simulate the bitter of the hop.

Carbazotic acid is a very common product of the action of nitric acid n organic substances; indigo, silk, and many resins furnish it in con- rable quantity. It is economically obtained in a pure state by the ion of nitric acid upon Botany Bay gum, but considerable quantities manufactured for the dyer by treating the crude carbolic acid from l tar with nitric acid. Carbazotic acid, as might be anticipated from composition, explodes when sharply heated, its carbon and hydrogen ng oxidised by the nitric peroxide.

When carbazotic acid is distilled with chloride of lime, it yields a heavy colourless oil having a very pungent odour of mustard, and boiling at 8° F.* This substance has been called *chloropicrine*, and has the re- rkable formula $C_2Cl_2(NO_4)$, which may be represented as formed upon type of marsh-gas, C_2H_4, in which three equivalents of the hydrogen replaced by chlorine, and the fourth by nitric peroxide. Chloro- rine is frequently met with among the products of the action of chlor- ting agents upon organic substances. It is almost insoluble in water, dissolves easily in alcohol and ether.

When an alcoholic solution of chloropicrine is acted on by sodium, it

* 233°·6 (Hofmann).

yields the subcarbonate of ethyle, and when treated with cyanide of sium, it exchanges two equivalents of chlorine for two of cyanogen ing an unstable dark red semi-fluid substance, having the com $C_2ClCy_2(NO_4)$, which may be regarded as derived from marsh-gas by the substitution of two equivalents of cyanogen, one equiv chlorine, and one equivalent of nitric peroxide, for the four equiv hydrogen.

It will be instructive to compare the composition of the most i members of the *phenyle series*, as that group of organic comp termed, which are derived from the hydrothetical radical phenyle (

Benzole or hydride of phenyle, .	$H(C_{12}H_5)$
Aniline or phenylamine, . .	$NH_2(C_{12}H_5)$
Phenic acid, ...	$HO.(C_{12}H_5)O$
Trinitrophenic or picric acid, .	$HO.[C_{12}H_2(NO_4)_3]O$

It is evident that whilst aniline may be regarded as ammonia the hypothetical phenyle is substituted for an equivalent of h phenic acid can be represented as formed from two equivalents by the substitution of phenyle for half the hydrogen, and benzo represented as a molecule of hydrogen, HH, in which one of the replaced by phenyle.

Some specimens of the kreasote found in commerce boil at temperature than carbolic acid; this is due to the presence o *acid* ($C_{14}H_8O_2$), corresponding to carbolic acid, but regarded as c the hypothetical radical kresyle ($C_{14}H_7$) in place of phenyle. Th in composition is attended with a resemblance in properties, fo acid has the same antiseptic property as carbolic acid, and is app similar purposes. When acted on by nitric acid, it yields *trinit acid* ($HO.C_{14}H_4(NO_4)_3O$), just as carbolic acid gives trinitroph ($HO.C_{12}H_3(NO_4)_2O$).

341. *Naphthaline.*—The most prominent constituent of the of coal tar is the napthaline, which is easily procured in a pure s the portions obtained at the close of the distillation, by simply the semisolid mass to remove any liquid hydrocarbons, and boi alcohol, from which the naphthaline crystallises on cooling in pearly flakes, which may be still further purified by the proces limation.

In itself naphthaline is not very interesting, being a remarkabl ent substance, but it has been made the subject of several be vestigations which have thrown much light upon the action of agents on organic compounds in general.

The most important of these researches is that upon the chlorine and bromine on naphthaline, which originated the now u accepted doctrine of substitution, and fully established the fac element may be replaced in a given compound by an equivalent of another element of a totally different chemical character.

Thus, by the action of chlorine upon naphthaline, the hydro moved in the form of hydrochloric acid, and there are obt new compounds by the progressive substitution of chlorin hydrogen, which Laurent distinguished by names indicating th of equivalents of chlorine present by means of the different vow last syllable, introducing a new penultimate syllable when t are exhausted, as will be seen in the following list:—

Naphthaline, .	$C_{20}H_8$	Chlonaphtuse, .	Wanting
Chlonaphtase, .	$C_{20}H_7Cl$	Chlonaphthalase, .	$C_{20}H_2Cl_6$
Chlonaphtese, .	$C_{20}H_6Cl_2$	Chlonaphthalese, .	Wanting
Chlonaphtise, .	$C_{20}H_5Cl_3$	Chlonaphthalise, .	$C_{20}Cl_8$.
Chlonaphtose, .	$C_{20}H_4Cl_4$		

will be observed that the original naphthaline type is here preserved ughout, the sum of the equivalents being always 28, and the number rbon equivalents 20.

ne of the most unexpected results of Laurent's investigation was the overy that some of these compounds may be obtained in several dis- t forms or modifications, which are isomeric, or have the same compo- n, but exhibit very different properties. Thus, there are seven varieties hlonaphtese, all containing $C_{20}H_6Cl_2$, and yet differing from each other uch as substances not having the same composition. Two of them liquids, and the five solid forms all fuse at different temperatures, ging between 88° and 214° F. Seven different forms of chlonaphtise wise exist, and four of chlonaphtose.

To account for this, Laurent supposed it to be by no means indifferent ich particle of hydrogen has been removed from the compound, believing h to have its assigned place and specific function. Thus it may easily conceived that the replacement of different particles of hydrogen by rine should give the seven modifications of chlonaphtese—

Naphthaline,	C_{20}HHHHHHHH
Chlonaphtese α,	C_{20}ClClHHHHHH
Chlonaphtese β,	C_{20}HHClClHHHH

so on. Other more recent investigations have given greater proba- y to this hypothesis.

Bromine, as might be anticipated, yields results similar to those with rine; but it could not have been predicted that substitution com- nds might be obtained in which one part of the hydrogen is replaced chlorine and the other by bromine. Thus, by acting upon a chlorine stitution compound with bromine, or *vice versâ*, the following sub- ces were produced:*—

Chlorebronaphtise,	$C_{20}H_5Cl_2Br$
Chlorebronaphtose,	$C_{20}H_4Cl_2Br_2$
Chloribronaphtose,	$C_{20}H_4Cl_3Br$
Bromechlonaphtuse,	$C_{20}H_3Br_2Cl_3$
Bromachlonaphtose,	$C_{20}H_4BrCl_3$

t will be observed that chloribronaphtose and bromachlonaphtose have same composition, though they possess different properties, and are ained in very different ways, the former being procured by the action of mine on chlonaphtise ($C_{20}H_5Cl_3$), and the latter by the action of chlorine n bronaphtese ($C_{20}H_6Br_2$). Another confirmation is thus obtained of belief, that upon the position of the hydrogen which is replaced, ends the character of the resulting compound.

Naphthaline is capable of direct union with chlorine to form two *orides of naphthaline*, having the formulæ $C_{20}H_8Cl_2$ and $C_{20}H_8Cl_4$,

* In naming these compounds, Laurent proceeded upon the same principle. The vowel iediately after the syllable *chlor-* or *brom-*, indicating the number of equivalents of that ent, whilst the vowel in the last syllable shows how many equivalents of hydrogen e been replaced. The name begins with *chlor-* when the compound has been obtained *he action of bromine upon a chlorine* substitution product, and *vice versâ*.

which may obviously be regarded as composed of substitution pr… combined with hydrochloric acid.

When acted upon by nitric acid, naphthaline furnishes three … tion products, in which one, two, and three equivalents of hy… replaced by NO_4; and each of these compounds, under the in… reducing agents, yields a base, just as nitrobenzole, under simil… ment, yields aniline.

By prolonging the action of boiling nitric acid upon naph… and evaporating the solution, crystals of *naphthalic* or *phthalic* … $2HO.C_{16}H_4O_6$, are obtained, which may be rendered anhydrous by … mation. Through this acid, naphthaline is connected with the ph… series; for when phthalic acid is heated with lime, it is resolved … carbonic acid and benzole—

$$\underset{\text{Phthalic acid.}}{2HO.C_{16}H_4O_6} + 4CaO = \underset{\text{Benzole.}}{C_{12}H_6} + 4(CaO.CO_2).$$

Moreover, by digesting phthalate of lime with hydrate of lime … elevated temperature for several hours, it is converted into benzoate … carbonate of lime—

$$\underset{\text{Phthalate of lime.}}{2CaO.C_{16}H_4O_6} + CaO.HO = \underset{\text{Benzoate of lime.}}{CaO.C_{14}H_5O_3} + 2(CaO.CO_2).$$

Paranaphthaline, $C_{30}H_{12}$, which is found among the last products of … distillation of coal tar, and has the same percentage composition as na… thaline, differs from that substance in being almost insoluble in alc… and fusing only at 356° F., whilst naphthaline fuses at 174° F.

Chrysene and *pyrene* are obtained at the close of the distillation of … tar; they are crystalline solids not possessing any special importance, … have also been observed among the products of the destructive distilla… of fatty and resinous bodies.

DESTRUCTIVE DISTILLATION OF WOOD.

342. The destructive distillation of wood may be advantageously studied in order to gain an insight into the effects of heat upon organic substances comparatively free from nitrogen, just as that of coal may serve as a general illustration of the behaviour of nitrogenised bodies under similar treatment.

The principal distinction between the two cases will be found to consist in the absence of basic substances from the products of the distillation of non-nitrogenised bodies.

All varieties of wood (freed from sap) consist essentially of *cellulose*, *lignine*, and mineral substances or ash. The cellulose ($C_{12}H_{10}O_{10}$) composes the wood-cells, and is therefore the most important constituent of the wood, the lignine being the material with which these cells are lined, and which appears to have a great influence upon the hardness of woods, being more abundant in the harder varieties, and particularly in such hard appendages as nut-shells. Lignine is far more easily dissolved by alkalies than cellulose, which is scarcely affected by them, but it has not hitherto been found possible to isolate the lignine in a state of purity for the purpose of determining its exact composition, since it is always accompanied in the wood by resinous matters, giving rise to the differences of

r in woods, and by a small quantity of nitrogenised matter, and of eposited with it from the sap.

e following results of the analysis of several woods will exhibit their al correspondence in composition :—

Wood dried in vacuo *at* 284° *F.*

	Beech.	Oak.	Birch.	Aspen.	Willow.
Carbon, ...	49·46	49.58	50·29	49·26	49·93
Hydrogen, ...	5·96	5·78	6·23	6·18	6·07
Oxygen, ...	42·36	41·38	41·02	41·74	39·38
Nitrogen, . . . } Sulphur, . . . }	1·22	1·23	1·43	0·96	0·95
Ash, ...	1·00	2·03	1·03	1·86	3·67
	100·00	100·00	100·00	100·00	100·00

ellulose in a nearly pure condition constitutes cotton, linen, and the kinds of (unsized) paper, since the processes to which the woody is subjected in the preparation of these materials, destroy and rate the less resistant lignine and the matters which accompany it.

n comparing the composition of wood with that of coal, it will be ous that the large proportion of oxygen in the former must give rise great difference in the products of destructive distillation. Accordy, it is found that water, carbonic oxide, carbonic acid, and acetic all highly oxidised bodies, are produced in large quantity, and that gaseous products of the distillation of wood burn with far less light those from coal, in consequence of the smaller proportion of the ier hydrocarbons.

he principal products of the action of heat upon wood are—

Wood Tar.

Solids.

Paraffine, . .	C_xH_x	Pyrene, . .	$C_{30}H_{12}$
Naphthaline, .	$C_{20}H_8$	Chrysene, . .	$C_{24}H_8$
Cedriret,		Resin,	
Pittacal,			

Liquids.

Toluole, . .	$C_{14}H_8$	Pyroligneous or acetic acid, .	$C_4H_4O_4$
Xylole, . .	$C_{16}H_{10}$	Wood naphtha, .	$C_2H_4O_2$
Cymole, . .	$C_{20}H_{14}$	Acetate of methyle,	$C_2H_3O.C_4H_3O_3$
Kreasote, . .	$C_{14}H_8O_2$	Formiate of methyle,	$C_2H_3O.C_2HO_3$
Picamar,		Acetone, . . .	$C_6H_6O_2$
Kapnomor, . .	$C_{20}H_{11}O_2$	Water,	
Eupione, . .	$C_{10}H_{12}$		

Gases.

Marsh-gas, ...	C_2H_4
Carbonic oxide, ...	CO
Carbonic acid, ...	CO_2

f these products, by far the most important are the pyroligneous acid, wood naphtha, and acetone.

The distillation of wood with a view to the preparation of th
stances, is conducted in the manner described in the section
charcoal (p. 57), when the distillate separates into two porti
heavier insoluble part constituting the wood tar, whilst the light
layer contains the pyroligneous acid, naphtha, and acetone.

On distilling this, the two last, boiling respectively at 150°
F., first distil over, and then the acetic acid, which boils at 243°
acid so obtained, however, is contaminated with tarry matte
communicate the peculiar odour of wood smoke, and adapt it
for the preservation of meat. In order to obtain pure acetic
crude acid is neutralised with carbonate of soda, and the aceta
thus obtained is moderately heated to expel the foreign substanc
then further purified by solution in water and crystallisation, a
tilled with sulphuric acid, which converts the soda into sulphat
the acetic acid to distil over.

343. *Wood naphtha—Methylic alcohol.*—In order to obtain
naphtha (or *proligneous ether*, or *wood spirit*, or *pyroxylic sp*
portion which distils over below 212° F. is rectified in a still c
chalk, which retains the acetic acid as acetate of lime.

The wood naphtha so obtained consists chiefly of *methyl*
($C_2H_4O_2$), but contains also acetone, acetate of methyle, and ce
substances which impart to it a peculiar odour, and cause it t
milky when mixed with water. Wood generally yields about o
naphtha to twenty of acetic acid. In order to obtain the pure
alcohol, chloride of calcium is dissolved to saturation in the cr
spirit, when a definite crystallisable compound is formed, of 2 e
of methylic alcohol and 1 of chloride of calcium, $CaCl.2C_2H_4O$
is heated in a retort, placed in a vessel of boiling water, as lo
acetone and acetate of methyle pass over, the above compound
decomposed at 212° F. An equal weight of water is then ad
residue in the retort, and the distillation continued, when the
alcohol distils over, accompanied by water, and the chloride o
remains in the retort. The diluted methylic alcohol is digested
time with powdered quick-lime, and again distilled, when it is o
a state of purity.

The useful applications of crude wood naphtha depend upon i
with a nearly smokeless flame in lamps (though as a source of
not of light), and upon its power of dissolving most resinous
employed in the preparation of varnishes, stiffening for hats, &c

Methylic alcohol is the first member of the very important h
series of alcohols, of which ordinary alcohol or spirit of wine i
and the consideration of which may be postponed until the
history of that alcohol shall have been studied. The desig
methylic alcohol supposes the existence in the pyroligneous
compound radical *methyle** (C_2H_3), of which methylic alcol
hydrated oxide = $(C_2H_3)O.HO$. This view is by no means ur
by experimental evidence; for if wood spirit be distilled with
of concentrated sulphuric acid, it yields a gas, the composition
is represented by the formula C_2H_3O, and this may be regar

* From *μέθυ, wine; ὕλη, wood.* The termination *-yle* is generally bestowe
und radicals, because *ὕλη* is put metaphorically for *matter*. Thus, *ethyle*
ply the matter from which ether compounds are derived.

ide of methyle. Again, if wood spirit be distilled with iodine and phorus, the hydriodic acid formed (*see* p. 175) acts upon the oxide of hyle, producing the compound C_2H_3I, *iodide of methyle*. When this eated in contact with zinc, iodide of zinc is produced, and a gas, ing the composition C_2H_3, which is that of the radical methyle, is ained. (This important question of compound radicals will be more y discussed hereafter.)

A sulphide, bisulphide, chloride, bromide, and cyanide of methyle, may o be obtained, as well as compounds of the oxide of methyle with sul- uric, nitric, acetic, &c., acids. The methyle series is, in fact, perfectly allel with the ethyle series, the members of which are far more important, d will therefore be more particularly considered hereafter.

One of the most interesting compounds derived from wood spirit is the *licylate of methyle*, or *oil of winter green* ($C_2H_3O \cdot C_{14}H_5O_5$), which is ex- acted from the flowers of the *Gaultheria procumbens*, and was one of the st vegetable products to be prepared artificially by the chemist. It is tained by distilling wood spirit with sulphuric acid and salicylic acid O . $C_{14}H_5O_5$), the latter acid being formed by the action of fused hydrate potash upon the salicine ($C_{26}H_{18}O_{14}$) extracted from willow bark.

It will be noticed that the compound of oxide of methyle (C_2H_3O) ith formic acid (C_2HO_3), or the *formiate of methyle*, $C_2H_3O \cdot C_2HO_3$, would ave the same *composition* as acetic acid, $HO \cdot C_4H_3O_3$, though they are ery different in *constitution*. An excellent illustration is here afforded f the distinction between an *empirical* and a *rational formula*, the former mply denoting the composition of a substance, without regard to the rrangement of its components, which is always indicated by the rational ormula. Thus, the empirical formula of acetic acid, as well as of ormiate of methyle, is $C_4H_4O_4$, but the rational formula of the latter is $C_2H_3O \cdot C_2HO_3$, showing it to consist of the oxide of methyle (C_2H_3O), ombined with formic acid (C_2HO_3), whilst the rational formula of acetic cid, $HO \cdot C_4H_3O_3$, represents it as a compound of water with *acetic nhydride* ($C_4H_3O_3$). Such compounds are often said to be *metameric*, the term *isomeric* being usually applied to compounds having the same composition, but which are not known to possess a different constitution, such as oil of turpentine and many of the essential oils.

344. *Paraffine* (C_nH_n), is a beautiful, semi-transparent, waxy substance, which distils over with the last portions of the tar from wood, and may be obtained in larger quantity by distilling peat, as well as from the mineral known as *Boghead cannel*. It is also found abundantly in the petroleum or mineral naphtha imported from Rangoon.

In order to extract the paraffine from wood tar, advantage is taken of its great resistance to the action of most chemical agents,* for which purpose the later portions of the distillate are moderately heated with concentrated sulphuric acid, which decomposes and chars most of the substances mixed with the paraffine, and allows the latter to collect as an oily layer upon the surface; this is allowed to cool and solidify, when it may be purified by pressure between blotting-paper, and solution in a hot mixture of alcohol and ether, from which it is deposited, on cooling, in brilliant plates.

Paraffine fuses at 110° F., and may be distilled at a higher temperature; it burns, like wax, with a very luminous flame, and is employed as a sub-

* *To which it owes its name, from parum, little; affinis, allied.*

stitute for wax in the manufacture of candles. It is insoluble in water, and dissolves sparingly in alcohol, ether being the best solvent for it.

It will be seen from the formula above given for paraffine, that the exact number of equivalents of carbon and hydrogen contained in it is unknown, since it does not form definite compounds with other substances, and therefore its exact equivalent weight cannot be ascertained; it is known, however, to contain an equal number of equivalents of carbon and hydrogen.

The substance known as *paraffine oil*, which is used for lubricating machinery, is the less volatile portion of the hydrocarbons obtained by the destructive distillation of Boghead cannel (found at Bathgate, near Edinburgh). The more volatile portion of the hydrocarbons so obtained is employed for illuminating purposes.

Acetone will be described hereafter.

Of the other products of the destructive distillation of wood enumerated at p. 466, some have been described amongst the products obtained from coal, and the remainder have been but little studied, and have not received any useful application.

Eupione ($C_{10}H_{12}$) is a liquid lighter than water, and boiling at 116° F.

Kapnomor is an oily liquid, which boils at 360°.

Picamar is another oily liquid, heavier than water.

Cedriret is a red crystalline substance.

Pittacal is a blue solid.

Stockholm tar is collected during the carbonisation of pine wood, containing a large quantity of resin, the tar running off through an aperture at the lower part of the pit, in which the imperfect combustion of the wood is carried on. It differs from ordinary tar in containing large quantities of resin and turpentine, the latter being separated from it by distillation, and the residue constituting the *pitch* of commerce.

Petroleum.—There are found, in different parts of the earth, generally in or near the coal-formations, several solid or liquid hydrocarbons, probably formed during the conversion of vegetable remains into coal, some of which have received useful applications.

The *Rangoon tar* has already been noticed as containing a considerable quantity of paraffine; the liquid part of this tar, after distillation and treatment with oil of vitriol to remove hydrocarbons of the benzole series,* is the liquid in which potassium and sodium are preserved; it is commonly called *petroleum* or *rock-oil*, and appears to be a mixture of several hydrocarbons. Petroleum is also employed occasionally as a solvent for caoutchouc and resinous substances. In the neighbourhood of the Caspian sea there are several springs from which rock-oil flows, together with water, from the surface of which it is skimmed and sent into commerce.

American petroleum.—Within the last few years abundant supplies of petroleum have been obtained from wells and springs in Pennsylvania and Canada, and the demand for it to serve as an illuminating agent, and for the lubrication of machinery, has created a new branch of commerce, giving rise to the rapid growth of "oil cities" in the neighbourhood of the wells. These rock-oils have a very peculiar unpleasant odour, and appear to consist chiefly of hydrocarbons belonging to the homologous series, of which marsh-gas (C_2H_4) is a member. Thus, the Pennsylvanian petroleum has furnished the hydrocarbons, C_8H_{10}, $C_{10}H_{12}$, $C_{12}H_{14}$, $C_{14}H_{16}$, $C_{16}H_{18}$, $C_{18}H_{20}$. In addition to these, the hydrocarbons, $C_{20}H_{30}$, $C_{22}H_{22}$, $C_{24}H_{24}$, homologous with olefiant gas (C_4H_4), have been obtained from it. Some of the mem-

* These hydrocarbons, when treated with oil of vitriol, form acids which are soluble in water. Thus benzole is converted into sulphobenzolic acid, $HO.C_{12}H_5.SO_2$.

s of the benzole series appear also to be present in the Canadian troleum.

The mineral substance known as *bitumen* or *asphaltum* contains a drocarbon, apparently isomeric with oil of turpentine, together with a sinous substance, and a black matter resembling pitch, and containing ygen. It is employed for making water-proof cements and black rnishes, being dissolved for this purpose in turpentine.

Bituminous shale, when distilled, furnishes products which, as far as ey are known, are closely allied to those obtained from wood and coal.

Oil of Turpentine and Substances Allied to it.

345. Turpentine is the generic name given to the viscous exudation btained by incising the bark of various species of pine. Several varieties f turpentine are met with in commerce, of which the two best known re the common turpentine which is obtained from the Scotch fir, and enice turpentine from the larch.

These are both solutions of *colophony* or common rosin ($C_{40}H_{30}O_4$) in he essential oil of turpentine ($C_{20}H_{16}$), and when distilled, yield from 5 to 90 per cent. of rosin, which remains in the retort, and from 25 to 0 per cent. of the essential oil, commonly sold as *spirits of turpentine*.

This essence of turpentine boils at 320° F., and floats upon water (sp. gr. 0·864), in which it is very sparingly soluble, its proper solvents being lcohol and ether. Its great inflammability renders it useful as a fuel for amps, but the large proportion of carbon which it contains causes it to burn with a smoky flame, rendering it necessary either to employ lamps onstructed especially to afford an extra supply of air to the flame, or to mix it with a certain proportion of alcohol. *Camphine* is distilled from the turpentine of the Boston pine.

The property of turpentine to dissolve resinous and fatty substances renders it exceedingly useful in the preparation of paints and varnishes, and for the removal of such substances from fabrics. It is also an excellent solvent for caoutchouc.

One of the most remarkable features of this essential oil is the facility with which it changes into isomeric or metameric modifications, exhibiting great differences in their physical and chemical properties.

When heated in a closed vessel to about 480° F. for some hours, oil of turpentine is converted into two isomeric modifications differing greatly from the original oil in the temperature at which they boil; for whilst oil of turpentine distils over entirely at 320 F°., one of these modifications, known as *isoterebenthene*, boils at 350° F., and the other, *metaterebenthene*, at 660°.

When digested, in the cold, with a small proportion of oil of vitriol, oil of turpentine yields *terebene* and *colophene*, the former boiling at 320° F., but differing from oil of turpentine in its odour, which resembles thyme, and in its want of action upon polarised light.

Colophene has a far higher boiling point (600°), and is much heavier than turpentine (sp. gr. 0·940), from which it is also distinguished by its indigo-blue colour when seen obliquely, though it is colourless by directly transmitted light. Moreover, the specific gravity of the vapour of colophene is 9·52, whilst that of turpentine is 4·76, or one-half that of colophene, rendering it probable that if the composition of turpentine be $C_{20}H_{16}$ (= 4 vols.), that of colophene is $C_{40}H_{32}$ (= 4 vols.), a relation expressed by saying that colophene is *polymeric* with turpentine. Colophene is also obtained by the distillation of colophony.

The ordinary oil of turpentine appears to be really itself a compound of two isomeric hydrocarbons, for when hydrochloric acid gas is passed into it, two distinct isomeric compounds are formed, both expressed by the formula, $C_{20}H_{16}.HCl$, but one *being a solid, and the other a liquid* even at 0° F.

The solid compound, which is known as *artificial camphor* or *hydrochlorate of dadyle*, forms white prismatic crystals very similar to camphor, and when its vapour is passed over heated quick-lime, the latter removes the hydrochloric acid, and the hydrocarbon known as *camphilene* or *dadyle* (δᾶς, a pine-torch) is obtained, which is isomeric with oil of turpentine, but boils at 273° instead of 320° F., and is without any action upon polarised light.

The liquid compound formed by the action of hydrochloric acid upon oil of turpentine is called *hydrochlorate of peucyle*; and when distilled with quick-lime yields *terebilene* or *peucyle* (πεύκη, *the pine*), also isomeric with oil of turpentine, but without action on polarised light.

Although oil of turpentine is not miscible with water, it is capable of forming three compounds with it in different proportions. When the oil is long kept in contact with water, crystals are deposited which have the composition $C_{20}H_{16}.6HO$; boiling water dissolves these, and deposits them in a prismatic form on cooling. The crystals fuse at about 217° F.; and when further heated, lose two equivalents of water, yielding another crystalline hydrate, which sublimes without alteration at about 480° F. When exposed to air this hydrate again absorbs two equivalents of water.

By distilling the aqueous solution of either of the preceding hydrates with a little sulphuric acid, a liquid hydrate smelling of hyacinths is obtained; it contains $C_{20}H_{16}.HO$, and is called *terpinole*.

When oil of turpentine is exposed to the air, it slowly becomes solid, absorbing oxygen, and becoming converted into resinous bodies.

Common rosin or *colophony.**—This substance is composed of two isomeric acids known as *sylvic* and *pinic*. When common rosin is treated with cold alcohol, the greater portion of it is dissolved; and if the alcohol be evaporated, it leaves an amorphous substance, which is *pinic acid*. The residue, left undissolved by cold alcohol, is dissolved by hot alcohol, and deposited in colourless prisms, which are *sylvic acid*. The salts of these acids have the composition $MO.C_{40}H_{29}O_3$, so that the acids themselves must be represented as $HO.C_{40}H_{29}O_3$. The pinate and sylvate of soda obtained by dissolving rosin in solution of soda or carbonate of soda, are largely used in the manufacture of yellow soap, and of the size for paper-makers. By distilling common rosin with the aid of superheated steam, it is obtained nearly free from colour.

346. *The turpentine series of hydrocarbons.*—Oil of turpentine is the representative of a large class of hydrocarbons, derived like itself from the vegetable kingdom, and all having a percentage composition corresponding to the formula $C_{20}H_{16}$. All the individuals of this group resemble turpentine in their liability to suffer conversion into isomeric modifications, in their solidification by absorption of oxygen when exposed to the air, in their combination with water to form crystalline hydrates, and above all, in their tendency to form artificial camphors by combining with hydrochloric acid.

The *oils of bergamotte, birch, camomile, carraway, cloves, hops, juniper, lemons, orange, parsley, pepper, savin, tolu, thyme*, and *valerian*, contain the same hydrocarbon $C_{20}H_{16}$, generally accompanied, in the natural oil, by the product of its oxidation, bearing a relation to the hydrocarbon similar to that which colophony bears to turpentine.

These essential oils are generally extracted from the flowers, fruit, leaves, or seeds, by distillation with water, the portion of the plant selected being suspended in the still by means of a bag or perforated vessel, so that there may be no danger of its being scorched by contact with the hot sides of the still, and so contaminating the distillate with *empyreumatic* matters (ἐμπυρεύω, to scorch). The water which distils over

* Colophon, a city of Ionia.

always holds a little of the essential oil in solution, and it is in this way that the fragrant distilled waters of the druggist are obtained. When the essential oil is present in large proportion, it collects as a separate layer upon the surface of the water, from which it is easily decanted. The oil which is dissolved in the water may be separated from it by saturating the liquid with common salt, when the oil rises to the surface, or by shaking it with ether, which dissolves the oil and separates from the water, the ethereal solution floating upon its surface, and leaving the oil when the ether is evaporated.

In cases like that of jasmine, where the delicate perfume of the flower would be injured by the heat, the flowers are pressed between woollen cloths saturated with oil of poppy seeds, which thus acquires a powerful odour of the flower.

Bisulphide of carbon is also sometimes employed as a solvent for extracting the essential oils.

Oil of peppermint contains a hydrocarbon called *menthene* ($C_{20}H_{18}$); *essence of cedar-wood* contains *cedrene* ($C_{32}H_{26}$).

347. *Camphors.*—Closely allied to the essential oils are the different varieties of camphor, which appear to be formed by the oxidation of hydrocarbons corresponding to the essential oils.

Common camphor ($C_{20}H_{16}O_2$) is found deposited in minute crystals in the wood of the *Laurus camphora* or camphor laurel, from which it is obtained by chopping up the branches and distilling them with water in a still, the head of which is filled with straw, upon which the camphor condenses. It is purified by subliming it in large glass vessels containing a little lime.

Camphor passes into vapour easily at the ordinary temperature of the air, and is deposited in brilliant octahedral crystals upon the sides of the bottles in which it is preserved. It fuses at 347° F. and boils at 399° F., and is very inflammable, burning with a bright smoky flame. It is sometimes dissolved in the oil used for the lamps of magic lanterns, to increase its illuminating power. Camphor is lighter than water (sp. gr. 0·996), and whirls about upon its surface in a remarkable way, dissolving meanwhile very sparingly (1 part in 1000), alcohol and ether being its appropriate solvents.

When distilled with anhydrous phosphoric acid, camphor loses two equivalents of water, and yields the hydrocarbon cymole ($C_{20}H_{14}$) homologous with benzole.

Borneo camphor ($C_{20}H_{18}O_2$) is obtained from the exudation of the *Dryobalanops camphora*. When this exudation is distilled, a hydrocarbon called *borneène* ($C_{20}H_{16}$), isomeric with oil of turpentine, first passes over, and afterwards the camphor, which is neither so fusible nor so volatile as ordinary camphor, and emits quite a different odour; it also crystallises in prisms instead of octahedra, and may be converted into ordinary camphor by the action of nitric acid, which oxidises two equivalents of hydrogen—

$$\underset{\text{Borneo camphor.}}{C_{20}H_{18}O_2} - H_2 = \underset{\text{Common camphor.}}{C_{20}H_{16}O_2}.$$

The Borneo camphor appears to have been formed by the combination of borneène with water, for if this hydrocarbon be distilled with solution of potash, it combines with two equivalents of water, and is converted into the camphor. On the other hand, when Borneo camphor is distilled with anhydrous phosphoric acid, it loses two equivalents of water, and yields borneène. It is interesting to remark that this hydrocarbon is also found in the essential oil of valerian.

The *oil of camphor* which accompanies the camphor distilled from the camphor laurel, contains an equivalent of oxygen less than common camphor, its formula being $C_{20}H_{16}O$.

348. *Balsams.*—The vegetable exudations known as balsams are mixtures of essential oils with resins and acids probably produced by the oxidation of the oils.

Balsam of Peru contains an oily substance termed *cinnamein* ($C_{54}H_{26}O_6$), a crystalline body, *styracine* ($C_{18}H_8O_2$), a crystalline volatile acid, the *cinnamic* ($C_{18}H_8O_4$), and a peculiar resin.

Balsam of Tolu also contains cinnamic acid and styracine, together with certain resins, which appear to have been formed by the oxidation of styracine.

Storax, also a balsamic exudation, contains the same substances, accompanied by a peculiar hydrocarbon, which has been named *styrole*, and has the composition $C_{16}H_8$. This liquid is characterised by a remarkable change which it undergoes when heated to about 400° F., being converted into a colourless solid, *metastyrole*, which is polymeric with styrole, into which it is reconverted by distillation.

349. *Resins.*—Colophony is the best known member of the class of resins, which are generally distinguished by their *resinous* appearance, fusibility, inflammability, burning with a smoky flame, insolubility in water, and solubility in alcohol.

As to their chemical composition, they are all rich in carbon and hydrogen, containing generally a small proportion of oxygen, and appear to have been formed, like colophony (p. 470), by the oxidation of a hydrocarbon analogous to turpentine.

Most of the resins also resemble colophony in their acid characters, their alcoholic solutions reddening blue litmus paper, and the resins themselves being soluble in the alkalies. This is the case with *sandarach* and *guaiacum resin*, the former of which contains three, and the latter two, resinous acids.

Copal appears to contain several resins, some neutral and some acid, and is distinguished by its difficult solubility in alcohol, in which it can be dissolved only after long exposure to the vapour of the solvent; but if it be exposed to the air for some time, at a moderately high temperature, it absorbs oxygen, and becomes far more easily soluble. Copal is readily dissolved by acetone. *Animi* and *elemi* resins are somewhat similar in properties to copal.

All these resins are used in the manufacture of varnishes.

Guaiacum resin is distinguished by its tendency to become blue under the influence of the more refrangible and chemically active (violet) rays of the solar spectrum, as well as under that of certain oxidising agents, such as chlorine and ozone.

Lac, so much used in the arts, belongs to the class of resins, being the exudation of certain tropical trees punctured by an insect. In its crude, natural state, encrusting the small branches, it is known as *stick-lac*, and has a deep red colour; when broken off the branches and boiled with water containing carbonate of soda, it furnishes a red colouring matter, very largely used in dyeing, leaving a resinous residue termed *seed-lac*, by fusing which the *shell-lac* is obtained. This resin is very complex, containing several distinct resinous bodies. It is largely used in the manufacture of hats, of sealing-wax, and of varnishes. The *lacquer* applied to brass derives its name from this resin, being an alcoholic solution of shell-lac, sandarach, and Venice turpentine. *Indian ink* is made by mixing lamp-black with a solution of 100 grains of lac in 20 grains of borax and 4 ounces of water.

fossil resinous substance, more nearly resembles this class of
any other, and contains several resinous bodies. It is distin-
ts insolubility, for alcohol dissolves only about one-eighth,
out one-tenth of it. After fusion, however, it becomes soluble
nd is used in this state for the preparation of varnishes.
guishing peculiarity of amber is, that it yields *succinic acid*,
$_6$ (*succinum*, *amber*), when digested with alkalies, distilled,
y nitric acid; in the latter case ordinary camphor is formed
time.
cid is also found in some of the resins of coniferous trees, and
of the wormwood. It is among the products of the action
d upon most fatty and waxy substances, and is present in
her fermented liquors, being produced during the fermenta-
. The acid is characterised by the cough-provoking vapour
ts when heated.
are prepared by dissolving resins in alcohol, or wood spirit,
a little turpentine or some fixed oil being added to prevent
n cracking when the solvent has evaporated. In order to
solution of the resin, it is usually powdered before being
the solvent, and mixed with coarsely powdered glass to pre-
becoming lumpy. *Methylated spirit* is now very generally
preparation of varnishes; it is simply spirit of wine, to
e wood naphtha has been added, to deter persons from drink-
prevent other frauds upon the Excise.
r gum benzoin, as it is erroneously called, is also a veget-
product, and is distin-
the presence of *benzoic*
$_{14}H_5O_3$), which may be
n it by heating the resin
earthen vessel (fig. 270)
a perforated sheet of
over which a drum or
is tied. When the heat
h is applied, benzoic acid
ur, and is condensed in
athery crystals in the
It may also be ex-
iling the resin with water
hen the benzoic acid is
the form of benzoate of

Fig. 270.

$_{14}H_5O_3$), and being but sparingly soluble in water, may be
by adding hydrochloric acid to the filtered solution.
id is generally recognised by its feathery appearance and
able odour, though this does not really belong to the acid,
e essential oil which is not easily separated; the vapour of
f is very irritating and produces coughing. It fuses when
eated, and burns with a smoky flame. Benzoic acid dissolves
parts of cold and 25 parts of boiling water. Alcohol and
e it easily.
of benzoic acid, or *benzoates*, have no practical importance,
viour of benzoic acid when distilled with an excess of lime

* *Acetone readily dissolves copal, mastic, and sandarach.*

or baryta has already been referred to as furnishing that important hydrocarbon, benzole (*see* p. 460).

OIL OF BITTER ALMONDS, AND ITS DERIVATIVES.—BENZOYLE SERIES.

350. Benzoic acid results from the oxidation of the essential oil of bitter almonds ($C_{14}H_6O_2$), which slowly absorbs two equivalents of oxygen from the air, and is converted into hydrated benzoic acid ($C_{14}H_6O_4$).

The formation of the essential oil of bitter almonds is one of the most interesting processes of vegetable chemistry.

Both the bitter and the sweet almond contain a large quantity of a fixed oil, which may be extracted from them by pressure, but which has no particular taste or odour, and differs entirely from the essential oil of bitter almonds, being, in fact, very similar to ordinary olive oil. The residue or almond-cake, which is left after expressing the oil, contains, in the case of the bitter almond only, a bitter principle, amounting to about $\frac{1}{50}$th of the weight of the almond, which may be extracted from the cake by hot alcohol, and may be crystallised from the solution; this substance is called *amygdaline*, and is represented by the formula $C_{40}H_{27}NO_{22}$, the crystals containing, in addition, six equivalents of water.

Now, if the residue left after extracting the amygdaline with alcohol be mixed with water and distilled, it does not yield any essential oil, although this may be obtained in abundance from the original cake after maceration in water, particularly if it be digested with water for several hours before distillation.

The sweet almond, which contains no amygdaline, does not afford any essential oil when distilled with water, showing that the amygdaline is really the source of the essence. Again, if boiling water be poured over the bitter almond cake, no essential oil is produced, even when the mixture is allowed to stand for some time, but if to this mixture there be added an emulsion of sweet almonds prepared with cold water, the bitter almond oil is at once formed, which is not the case, however, if the emulsion be prepared with boiling water.

From this it is evident that a substance exists in both sweet and bitter almonds which is capable of developing the essence from the amygdaline contained in the latter, but which loses its power when acted upon by hot water. This may be still further proved by dissolving pure amygdaline in water, and adding an emulsion of sweet almonds, when the essence is at once produced.

When the emulsion of sweet almonds is filtered and mixed with alcohol, a white substance resembling albumen is precipitated, which contains carbon, hydrogen, nitrogen, and oxygen, and very easily putrefies when exposed to the air in a moist state. If this substance, which is called *emulsine* or *synaptase* (συνάπτω, *to bring into action*), be dissolved in cold water, and mixed with a solution of amygdaline, the oil of bitter almonds is soon formed in abundance, but if the solution of emulsine be boiled, it is no longer capable of developing the essence. On examining the solution of amygdaline in which the essential oil has been produced by the action of emulsine, it is found to contain, in addition, hydrocyanic acid (C_2HN), grape-sugar ($C_{12}H_{14}O_{14}$), and formic acid ($C_2H_2O_4$), so that the decomposition may be thus represented—

$$\underset{\text{Amygdaline.}}{2C_{40}H_{27}NO_{22}} = \underset{\substack{\text{Bitter almond}\\ \text{oil.}}}{4C_{14}H_6O_2} + \underset{\substack{\text{Hydrocyanic}\\ \text{acid.}}}{2C_2HN} + \underset{\text{Grape sugar.}}{C_{12}H_{14}O_{14}} + \underset{\substack{\text{Formic}\\ \text{acid.}}}{4C_2H_2O_4} + 6HO.$$

formation of the essential oil of bitter almonds must be regarded, ore, as dependent upon a species of fermentation or metamorphosis bitter principle amygdaline, induced by contact with an albuminous nce, emulsine, itself very prone to undergo decomposition when ed to air in the presence of moisture.

s essential oil may also be obtained from laurel leaves, and from the ls of most stone fruit.

ien the oil of bitter almonds is distilled over, it is accompanied by drocyanic acid formed at the same time, and it is this which renders dinary commercial oil so powerful a poison, for if it be purified by ation from a mixture of lime and chloride of iron (see *Prussian blue*), retains the hydrocyanic acid, it becomes comparatively harmless. ter process for obtaining the pure oil of bitter almonds consists in ng the crude oil with an equal volume of a strong solution of bisul- of soda, with which it forms a white crystalline compound. If this tilled with solution of carbonate of soda, the pure oil passes over.

poisonous properties of laurel-water, and similar preparations, are ue to the presence of hydrocyanic acid.

crude essential oil of bitter almonds also contains a crystalline substance benzoine ($C_{28}H_{12}O_4$), which is interesting as being polymeric with the essence, hich it may be converted by passing its vapour through a red-hot tube. The il may be entirely converted into this substance by shaking it with an alco- olution of potash.

n the pure essential oil of bitter almonds ($C_{14}H_6O_2$) is acted upon by dry e, it evolves hydrochloric acid, and becomes converted into a colourless liquid, an odour of horse-radish, and containing $C_{14}H_5ClO_2$, 1 equivalent of hydro- ving been removed, and its place filled by an equivalent of chlorine. If this be acted upon by the bromides, iodides, cyanides, or sulphides of the metals, orine is removed in its turn, the vacancy being filled up by bromine, iodine, en or sulphur, compounds being obtained which have the formulæ—

$$C_{14}H_5BrO_2$$
$$C_{14}H_5IO_2$$
$$C_{14}H_5CyO_2$$
$$C_{14}H_5SO_2$$

n boiled with water, this chlorine compound exchanges its chlorine for the of the water, and is converted into hydrated benzoic acid—

$$C_{14}H_5ClO_2 + 2HO = C_{14}H_5O_3.HO + HCl.$$

omparing the composition of these compounds with that of the essential oil hich they are derived, our attention is called to the existence of $C_{14}H_5O_2$ in hem—

Oil of bitter almonds, .	$(C_{14}H_5O_2)H$
Benzoic acid, . . .	$(C_{14}H_5O_2)O.HO$
Chlorine compound, .	$(C_{14}H_5O_2)Cl$
Bromine „ . .	$(C_{14}H_5O_2)Br$, &c.

circumstance led many chemists to assume the existence in these com- of the radical benzoyle ($C_{14}H_5O_2$). capable of playing the part of an ele- y substance in uniting with oxygen, chlorine, &c., and therefore resembling ments in its chemical tendencies, from which resemblance it is spoken of as a lement or compound radical.

is radical be represented by Bz, the formation of the members of the *benzoyle* om oil of bitter almonds will be simply and easily traced.

Oil of bitter almonds, *hydride of benzoyle*, .	BzH
Benzoic acid, *hydrated oxide of benzoyle*, .	BzO.HO
Chloride of benzoyle, ...	BzCl
Bromide „	BzBr
Iodide „	BzI
Cyanide „	BzCy
Sulphide „	BzS

The radical benzoyle itself has been recently obtained in a separate state by the action of sodium on chloride of benzoyle. It forms prismatic crystals, which fuse easily, and may be sublimed without decomposition. They are sparingly soluble in alcohol and ether. The formula $C_{14}H_5O_2$ should be doubled to express correctly a molecule of this radical (*see Alcohol radicals*).

It will be noticed that the compound BzO, or *anhydrous benzoic acid*, is not included in the above enumeration of the benzoyle series. A compound polymeric with this, and which may be represented as Bz_2O_2 (or $C_{14}H_5O_2 \cdot C_{14}H_5O_2$), is obtained by heating benzoate of soda with chloride of benzoyle—

$$NaO \cdot BzO + BzCl = NaCl + BzO \cdot BzO .$$

This substance, which is called *benzoic anhydride*, has no acid properties whatever. It does not dissolve in cold water, but if boiled with water, is slowly converted into hydrated benzoic acid.

When oil of bitter almonds is decomposed by hydrate of potash dissolved in alcohol, it yields *benzoic alcohol* ($C_{14}H_6O_2$), which will be more particularly noticed hereafter.

351. Very closely connected with the essential oil of bitter almonds are the essences of cinnamon and cassia, which consist chiefly of an oxidised essence, represented by the formula $C_{18}H_8O_2$, and convertible by boiling with nitric acid into the essence of almonds. By heating the essence of cinnamon with hydrate of potash, it is oxidised and converted into cinnamate of potash—

$$\underset{\text{Oil of cinnamon.}}{C_{18}H_8O_2} + KO \cdot HO = \underset{\text{Cinnamate of potash.}}{KO \cdot C_{18}H_7O_2} + H_2 .$$

On dissolving this salt in water, and adding an acid, the *cinnamic acid* is precipitated in feathery flakes, closely resembling benzoic acid, both in appearance and chemical characters.

The same reasons exist as in the case of the benzoyle series, for assuming the existence, in the compounds derived from oil of cinnamon, of the radical *cinnamyle*, $C_{18}H_7O_2$, so that the oil of cinnamon would be a hydride of cinnamyle ($C_{18}H_7O_2$)H, and cinnamic acid the hydrated oxide of that radical ($C_{18}H_7O_2$)O . HO.

Essential oil of cummin is a mixture of the hydrocarbon cymole ($C_{20}H_{14}$), which has been already noticed, with an oxidised essence, $C_{20}H_{12}O_2$, which is closely analogous to those of almonds and cinnamon, and is called *hydride of cumyle* ($C_{20}H_{11}O_2$)H; when acted upon by oxidising agents it yields *cuminic acid* (HO . $C_{20}H_{11}O_2$), which resembles benzoic acid, but is characterised by an odour similar to that of the bug. From the hydride of cumyle an oily compound has been obtained, which is polymeric with the supposed radical *cumyle*, having the composition $C_{40}H_{22}O_4$, and that it is really composed of a double equivalent of that radical is rendered very probable by its behaviour when fused with hydrate of potash, since water is then decomposed, its hydrogen converting one equivalent of cumyle into hydride of cumyle, whilst its oxygen converts the other equivalent into cuminic acid—

$$C_{40}H_{22}O_4 + (KO \cdot HO) = \underset{\text{Hydride of cumyle.}}{(C_{20}H_{11}O_2)H} + \underset{\text{Cuminate of potash.}}{KO \cdot (C_{20}H_{11}O_2)O} .$$

The essential oils of *aniseed*, *fennel*, and *tarragon* contain, in addition to a hydrocarbon isomeric with turpentine, a solid crystalline oxidised essence ($C_{20}H_{12}O_2$) isomeric with the hydride of cumyle. That this substance is not hydride of cumyle however, is at once proved by the action of oxidising agents, which convert it into *hydride of anisyle*, ($C_{16}H_7O_4$)H, and *anisic acid*, HO . $C_{16}H_7O_3$, the latter being isomeric with winter-green oil (*see* p. 467).

352. SALICINE AND ITS DERIVATIVES—GLUCOSIDES.—*Oil of spiræa, meadow sweet*, consists chiefly of the compound ($C_{14}H_6O_4$) isomeric with hydrated benzoic acid; this compound is easily obtained artificially by the oxidation of *salicine*, a bitter substance extracted from willow bark by boiling it in water, removing the colouring matter and tannin from the solution by boiling with hydrated oxide of lead, precipitating the excess of lead by hydrosulphuric acid, and evaporating the filtered liquid when the salicine crystallises out, and may be obtained by recrystal-

from alcohol, in beautiful white needles having the composition $C_{26}H_{18}O_{14}$.

Salicine is sparingly soluble in cold water and insoluble in ether, but solves readily in boiling water and in alcohol. It is readily distinguished the red colour which it gives with concentrated sulphuric acid, which nifests its presence when applied to the inner bark of the willow. hen distilled with dilute sulphuric acid and bichromate of potash, it lds the oil of spiræa.

The changes suffered by salicine when boiled with a dilute mineral acid (as sulric) are very remarkable, for after the boiling has been continued for a few utes, the solution is found to contain grape-sugar, together with a crystalline stance called *saligenine*, which is distinguished by the intense blue colour which ives with perchloride of iron. The change is easily explained, for the addition 4 equivalents of water to salicine would provide the elements of grape-sugar and genine—

$$\underset{\text{Salicine.}}{C_{26}H_{18}O_{14}} + 4HO = \underset{\text{Saligenine.}}{C_{14}H_8O_4} + \underset{\text{Grape-sugar.}}{C_{12}H_{14}O_{14}}.$$

Emulsine or synaptase is capable of effecting this change in salicine, and it will remembered that grape-sugar is one of the products of the action of that ferment n amygdaline. If the ebullition with the diluted acid be continued for a length time, the liquid deposits a resinous substance, *saliretine*, which is isomeric with of bitter almonds ($C_{14}H_6O_2$).

A very striking example of the stability of types, notwithstanding the substitution one element for another, is found in the circumstance that salicine, under the uence of chlorine, yields three different products containing chlorine in place hydrogen, and that when these are boiled with dilute acids, they yield other prots containing chlorine, and bearing the same relation to their chlorinated primitive ich saligenine and saliretine respectively bear to salicine.

Thus we have—

Salicine, . . . $C_{26}H_{18}O_{14}$	Saligenine, . . . $C_{14}H_8O_4$
Chlorosalicine, . $C_{26}\left\{\begin{matrix}H_{17}\\Cl\end{matrix}\right\}O_{14}$	Chlorosaligenine, . $C_{14}\left\{\begin{matrix}H_7\\Cl\end{matrix}\right\}O_4$
Dichlorosalicine, . $C_{26}\left\{\begin{matrix}H_{16}\\Cl_2\end{matrix}\right\}O_{14}$	Dichlorosaligenine, $C_{14}\left\{\begin{matrix}H_6\\Cl_2\end{matrix}\right\}O_4$
Trichlorosalicine, $C_{26}\left\{\begin{matrix}H_{15}\\Cl_3\end{matrix}\right\}O_{14}$	Trichlorosaligenine, $C_{14}\left\{\begin{matrix}H_5\\Cl_3\end{matrix}\right\}O_4$

When salicine is fused with hydrate of potash, the mass dissolved in water, and drochloric acid added, beautiful needles of *salicylic acid* ($HO.C_{14}H_5O_5$) are arated. This acid may also be obtained from the oil of spiræa by a similar cess, and it will be seen that salicylic acid bears the same relation to this oil benzoic acid bears to oil of bitter almonds—

Oil of bitter almonds, $C_{14}H_6O_2$	Oil of spiræa, . . . $C_{14}H_6O_4$
Benzoic acid, . . . $C_{14}H_6O_4$	Salicylic acid, . . . $C_{14}H_6O_6$

Salicylic acid has been obtained in a most interesting manner by the simultaneous ion of carbonic acid and sodium upon phenole—

$$\underset{\text{Phenole.}}{C_{12}H_6O_2} + 2CO_2 + Na = \underset{\text{Salicylate of soda.}}{NaO.C_{14}H_5O_5} + H.$$

Exactly as chemists have been led to consider the bitter almond oil as hydride of nzoyle, so they have regarded oil of spiræa as *hydride of salicyle* ($C_{14}H_5O_4.H$), assumg the existence of the radical *salicyle* ($C_{14}H_5O_4$), of which salicylic acid would be hydrated oxide. We find this view of the constitution of these compounds supted by the circumstance, that when the oil of spiræa is heated with chloride of nzoyle, a substance is obtained which may be regarded as composed of the two dicals salicyle and benzoyle—

$$\underset{\text{Oil of spiræa.}}{C_{14}H_5O_4.H} + \underset{\text{Chloride of benzoyle.}}{C_{14}H_5O_2.Cl} = \underset{\text{Benzoyle-salicyle.}}{C_{14}H_5O_2.C_{14}H_5O_4} + HCl.$$

From a careful study of the behaviour of salicine under the action of various agents, the inference has been drawn that it is a compound of saligenine ($C_{14}H_8O_4$) with a substance ($C_{12}H_{10}O_{10}$), which becomes converted into grape-sugar, by assimilation of water, as soon as it is separated from the saligenine.

Salicine is occasionally employed in medicine as a febrifuge, and is a common adulteration of quinine.

Salicine is the chief member of the class of substances termed *glucosides* from the presence of grape-sugar (glucose) among their products of decomposition. To this class belong several other substances much resembling salicine, and, like it, extracted from the barks of different trees.

353. *Populine* ($C_{40}H_{22}O_{16}$) is a sweet crystalline substance obtained from the bark and leaves of the aspen, and especially interesting from its close connection with the benzoyle and salicyle series; for when boiled with solution of baryta, it is decomposed into benzoic acid (which unites with the baryta) and salicine—

$$\underset{\text{Populine.}}{C_{40}H_{22}O_{16}} + BaO.HO = \underset{\text{Benzoate of baryta.}}{BaO.C_{14}H_5O_3} + \underset{\text{Salicine.}}{C_{26}H_{18}O_{14}}.$$

Nor is this the only connecting link, for populine yields oil of spiræa when distilled with sulphuric acid and bichromate of potash, and when boiled with dilute acids furnishes benzoic acid, saliretine, and grape-sugar—

$$\underset{\text{Populine.}}{C_{40}H_{22}O_{16}} + 4HO = \underset{\text{Benzoic acid.}}{HO,C_{14}H_5O_3} + \underset{\text{Saliretine.}}{C_{14}H_6O_2} + \underset{\text{Grape-sugar.}}{C_{12}H_{14}O_{14}}.$$

In order to explain this production of benzoyle and salicyle compounds from populine, it is usual to regard this substance as formed from salicine ($C_{26}H_{18}O_{14}$) by the introduction of an equivalent of benzoyle ($C_{14}H_5O_2$), in the place of an equivalent of hydrogen—

$$\underset{\text{Populine.}}{C_{40}H_{22}O_{16}} = \underset{\text{Benzoyle-salicine.}}{C_{26}H_{17}(C_{14}H_5O_2)O_{14}}.$$

Phloridzine ($C_{42}H_{24}O_{20}$) is extracted from the bark of the apple, pear, plum, cherry tree; it crystallises readily, is slightly bitter, and when boiled with dilute acids, yields grape-sugar and a resinous substance called *phloretine* ($C_{30}H_{14}O_6$). Its most interesting property is that of forming a red compound (*phloridzeine*) when exposed to the joint influences of air and ammonia—

$$\underset{\text{Phloridzine.}}{C_{42}H_{24}O_{20}} + O_6 + 2NH_3 = \underset{\text{Phloridzeine.}}{C_{42}H_{30}N_2O_{26}}.$$

This red compound combines with ammonia to form a purple mass with a copper lustre, which dissolves in water with a fine blue colour. The production of colouring matter from phloridzine is an excellent example of that conjoined action of air and ammonia by which certain natural colouring matters, such as litmus, are formed from substances which are themselves destitute of colour.

Quercitrine ($C_{36}H_{18}O_{20}$) is the yellow colouring matter extracted by alcohol from the bark of the quercitron. It is a crystallisable substance, and is decomposed by boiling with acids into grape-sugar and a yellow crystalline body called *quercetine*—

$$\underset{\text{Quercitrine.}}{C_{36}H_{18}O_{20}} + 4HO = \underset{\text{Quercetine.}}{C_{24}H_8O_{10}} + \underset{\text{Grape-sugar.}}{C_{12}H_{14}O_{14}}.$$

Esculine ($C_{42}H_{24}O_{26}$) is extracted from the bark of the horse-chestnut by boiling water. If the tannin and colouring matter be precipitated from the infusion by acetate of lead, the filtered liquid treated with sulphuretted hydrogen to remove the excess of lead, and the solution, after a second filtration, evaporated, the esculine is obtained in colourless needles. It is remarkable for its *fluorescence*; although the solution is colourless by transmitted light, it appears of a beautiful deep blue colour when viewed at certain angles. This substance is also a glucoside, for when boiled with dilute acids, it yields grape-sugar and a crystalline substance known as *esculetine*.

$$\underset{\text{Esculine.}}{C_{42}H_{24}O_{26}} + 10HO = \underset{\text{Esculetine.}}{C_{18}H_6O_8} + \underset{\text{Grape-sugar.}}{2C_{12}H_{14}O_{14}}.$$

Paviine also occurs in the horse-chestnut bark, but in far larger quantity

of the ash. It is distinguished from esculine by exhibiting a green escence.

Saponine is a substance closely allied to the glucosides, and is found in the soap-t, the fruit of the horse-chestnut, the pimpernel, the root of the pink, and in y other plants. It may be extracted by boiling alcohol, which deposits it in an orphous state on cooling. Saponine is soluble in water, and its solution is cha-terised by the readiness with which it lathers, like soap and water, although it y contain a very small quantity of saponine. This property leads to the use of ections containing it, such as those of the soap-wort, and of the soap-nut of dia, for the purpose of cleansing certain delicate fabrics.

Picrotoxine ($C_{24}H_{14}O_{10}$?) is a crystalline substance, to which the poisonous pro-rties of *Cocculus indicus* are due. It appears to have feeble acid tendencies, and extracted from an acidified solution by shaking with ether. On evaporating the ereal solution it leaves prismatic needles of an intensely bitter taste.

354. ESSENTIAL OILS CONTAINING SULPHUR—ALLYLE SERIES.—The essen-l oils of *asafœtida*, of *cress*, *garlic*, *horseradish*, *leeks*, *mustard*, *onions*, d *radishes*, differ from those which have been already described by con-ining sulphur.

Those of asafœtida, cress, garlic, leeks, onions, and radishes, are com-sed essentially of the same substance, represented by the formula H_3S. The essence of mustard and that of horseradish are composed of H_3NS_2.

The chemistry of the origin of essential oil of mustard is analogous to at of essence of almonds. The oil is obtained from the seeds of the ack mustard after removing the fixed oil (which has no pungency what-er) by pressure; on moistening the crushed seed with water, the pro-ction of the essential oil is indicated by its peculiar odour, and it may separated from the seeds by distillation. The mustard seeds con-in a salt of potash with a peculiar acid called *myronic acid*,* (HO . $C_{20}H_{19}NS_4O_{18}$), together with a substance similar to the emulsine of monds, which has been termed *myrosine*, and is capable of inducing the composition of the myronic acid, and the consequent production of sence of mustard, just as the emulsine of almonds developes the essential by the decomposition of the amygdaline; in the case of mustard, how-er, the nature of the decomposition has not been so clearly made out, t is probably represented by the equation—

$$\underset{\text{Myronic acid.}}{HO . C_{20}H_{19}NS_4O_{18}} = \underset{\text{Essence of mustard.}}{C_8H_5NS^2} + \underset{\text{Glucose.}}{C_{12}H_{14}O_1{}^4} + HO + 2SO_2 .$$

The essence of mustard has been produced artificially in a very inter-ting and remarkable manner.

When glycerine (the sweet principle of the fats and fixed oils) is dis-lled with the biniodide of phosphorus, a colourless ethereal liquid is ob-ined, which has the composition C_6H_5I, and is called *iodide of allyle*, cause when distilled with sodium, it yields iodide of sodium and a latile liquid composed of C_6H_5, and called allyle, in allusion to its pecu-r odour (*allium*, *garlic*). The formation of iodide of allyle is explained the following equation—

$$\underset{\text{Glycerine.}}{C_6H_8O_6} + PI_3 = \underset{\text{Iodide of allyle.}}{C_6H_5I} + PO_3 + 3HO + I .$$

When iodide of allyle is distilled with sulphocyanide of potas-m, an oily liquid is obtained, identical in properties and composition

* From μύρον, an unguent.

with oil of mustard, which must therefore be regarded as a *sulphocyanide of allyle*, its artificial production being thus explained—

$$\underset{\text{Iodide of allyle.}}{C_6H_5I} + \underset{\text{Sulphocyanide of potassium.}}{K(C_2NS_2)} = \underset{\text{Sulphocyanide of allyle, or oil of mustard.}}{C_6H_5.C_2NS_2} + KI.$$

Additional interest is created in this artificial formation of oil of mustard when it is found to be convertible into oil of garlic, by being heated with sulphide of potassium, when sulphocyanide of potassium is formed at the same time, thus—

$$\underset{\text{Essence of mustard.}}{C_6H_5.C_2NS_2} + KS = \underset{\text{Essence of garlic.}}{C_6H_5.S} + \underset{\text{Sulphocyanide of potassium.}}{K(C_2NS_2)}.$$

Hence it is inferred that the essence of garlic is a *sulphide of allyle*, of which essence of mustard is a sulphocyanide.

A considerable number of compounds are included in the *allyle series*, but are not at present possessed of any practical importance.

The *allylic alcohol* ($C_6H_5O.HO$) is interesting as the prototype of a new class of alcohols, parallel with that represented by common alcohol ($C_4H_5O.HO$). In order to obtain it, the iodide of allyle is decomposed by oxalate of silver, when oxalate of allyle is obtained—

$$\underset{\text{Iodide of allyle.}}{C_6H_5I} + AgO.C_2O_3 = \underset{\text{Oxalate of allyle.}}{C_6H_5O.C_2O_3} + AgI.$$

By treating oxalate of allyle with ammonia, allylic alcohol and oxamide are obtained—

$$\underset{\text{Oxalate of allyle.}}{C_6H_5O.C_2O_3} + NH_3 = \underset{\text{Allylic alcohol.}}{C_6H_5O.HO} + \underset{\text{Oxamide.}}{C_2H_2NO_2}$$

Allylene (C_6H_4), the olefiant gas of the allyle series, is homologous with acetylene (C_4H_2), and much resembles it in its chemical relations. It has been prepared by heating chlorinated propylene in a sealed tube with sodium-alcohol. The chlorinated propylene is a product of the action of pentachloride of phosphorus upon acetone—

$$\underset{\text{Acetone.}}{C_6H_6O_2} + PCl_5 = \underset{\text{Chlorinated propylene.}}{C_6H_5Cl} + HCl + PCl_3O_2;$$

$$C_6H_5Cl + \underset{\text{Sodium-alcohol.}}{C_4H_5NaO_2} = \underset{\text{Allylene.}}{C_6H_4} + NaCl + \underset{\text{Alcohol.}}{C_4H_6O_2}.$$

By its action on ammoniacal nitrate of silver, it yields *argentallylene*, C_6H_3Ag. When sodium is heated in allylene, carbon and hydrogen are liberated, and sodic acetylide is formed, $C_6H_4 + Na_2 = C_4Na_2 + C_2 + H_4$, a little propylene ($C_6H_6$) is formed at the same time.

355. GUM-RESINS.—The *gum-resins* consist of a mixture of gum with resin, and occasionally with essential oil, and are distinguished by their behaviour when triturated with water, which dissolves the gum and leaves the oil and resin suspended, giving the liquid a milky appearance. They also differ from most resins in being only partially soluble in alcohol. The gum-resins exude from the plants producing them in a milky state, gradually solidifying by exposure to the air.

Asafœtida contains a resin of the composition $C_{40}H_{28}O_{10}$, and owes its powerful odour to an essential oil containing sulphur, which has been already noticed. *Galbanum*, *ammoniacum*, *aloes*, *olibanum* or *frankincense*, *scammony*, *gamboge*, *myrrh*, and *euphorbium*, also belong to the class of gum-resins.

Caoutchouc (C_5H_4) is so far allied to the gum-resins, that it is procured from a milky exudation furnished by several tropical plants, particularly the *Hævæa guianensis* and Jatropha elastica. Incisions are made in

se trees, and the milky liquid thus obtained is spread upon a clay
tle-shaped mould, which is then suspended over a fire; a layer of
utchouc is thus deposited upon the mould, and its thickness is after-
ds increased by repeated applications of the milky liquid, the mould
ng eventually broken out of the caoutchouc bottle thus formed. The
k colour of the caoutchouc found in commerce is believed to be due
he smoke from the fire over which it is dried, for pure caoutchouc is
ite, and may be obtained in this state by dissolving in washed ether
precipitating it by the addition of alcohol, in which it is insoluble.
e caoutchouc of commerce contains a small quantity of albumen, derived
m the original milky liquid, this being really a solution of albumen
ding in suspension about 30 per cent. of caoutchouc, which rises to the
face like cream, when the juice is diluted with water and allowed to
id, becoming coherent and elastic when exposed to air. It will be re-
mbered that many of the chief uses of caoutchouc depend upon its
sical rather than its chemical properties, its lightness (sp. gr. 0·93)
impermeability to water adapting it for the fabrication of waterproof
les of clothing, of life-buoys, &c., whilst its remarkable elasticity gives
to a still greater variety of applications.

For the manufacture of waterproof cloth, caoutchouc is dissolved in
ified turpentine, and the solution is spread, in a viscid state, over the
faces of two pieces of cloth of the same size, which are then laid face
face and passed between rollers, the pressure of which causes perfect
esion between the two surfaces. Bisulphide of carbon, benzole, and
naphtha, pertroleum, the oils, both fixed and volatile, are also
able of dissolving caoutchouc.

Marine glue is a solution of caoutchouc with a little shell-lac in coal
naphtha.

Waterproof felt is made by matting together fibres of cotton im-
gnated with a solution of caoutchouc in naphtha, and passing the felt
ween rollers. When kept for a length of time, its strength and water-
of qualities are deteriorated, in consequence of the oxidation of the
utchouc, which is thus converted into a resinous substance resembling
ll-lac, and easily dissolved by alcohol.

The alkalies and diluted acids are without effect upon caoutchouc.
hen gently warmed, it becomes far more soft and pliable; it fuses at
ut 250° F., and is converted into an oily liquid which becomes viscid
cooling, but will not again solidify, and is useful for lubricating stop-
ks. When further heated in air, it burns with a bright smoky flame.
ated in a retort, caoutchouc is decomposed into several hydrocarbons,
of which, called *isoprene*, boils at about 100° F., and has the com-
ition $C_{10}H_8$, while *caoutchine* has the same composition as oil of
pentine, and boils at 340° F.; they are well adapted for dissolving
utchouc.

Vulcanised caoutchouc is produced by incorporating this substance with
r 3 per cent. of sulphur, which not only increases in a remarkable
nner its elasticity, but prevents it from cohering under pressure, and
m adhering to other surfaces unless strongly heated. The vulcanised
utchouc is also insoluble in turpentine and naphtha. Ordinary vul-
nised caoutchouc generally contains more sulphur than is stated above,
ich causes it to become inelastic and brittle after it has been some
ne in use; and for some purposes, such as the manufacture of overshoes,
is found advantageous to add some carbonate of lead as well as sulphur.

When a sheet of caoutchouc is allowed to remain for some time in fused sulphur at 250° F., it absorbs 12 or 15 per cent. of that element without suffering any material alteration; but if it be heated for a short time to 300° F., it becomes vulcanised; and when still further heated, is converted into the black horny substance called *vulcanite* or *ebonite*, and used for the manufacture of combs, &c. By treating the vulcanised caoutchouc with sulphite of soda, the excess of sulphur above 2 or 3 per cent. may be dissolved out.

There are several processes employed for the manufacture of vulcanised caoutchouc; sometimes the sulphur is simply incorporated with it by mechanical means. Another process consists in immersing the caoutchouc in a mixture of 100 parts of bisulphide of carbon with 2·5 parts of chloride of sulphur (S_2Cl),* or in dissolving the sulphur in oil of turpentine, which is afterwards used to dissolve the caoutchouc. When the turpentine has evaporated, a mixture of caoutchouc and sulphur is left, which may easily be moulded into any desired form, and afterwards vulcanised by exposure to high pressure steam, having a temperature of about 280° F.

The true chemical constitution of vulcanised caoutchouc is not yet understood; it has been suggested that the sulphur has been substituted for a portion of the hydrogen in the original caoutchouc, but it does not seem improbable that this hydrocarbon may combine directly with sulphur.

Caoutchouc is by no means rare in the vegetable world, being found in the milky juices of the poppy (and thence in opium), of the lettuce, of the euphorbium and asclepia families.

Gutta percha, like caoutchouc, is originally a milky juice which exudes from incisions made into the wood of the *Isonandra percha*, a native of the Eastern archipelago. This juice soon solidifies when exposed to air, to a brownish mass heavier than caoutchouc (sp. gr. 0·98), and differing widely from it by being tough and inelastic at the ordinary temperature, becoming quite soft and plastic when heated nearly to the boiling point of water. Being impervious to water, it is employed as a waterproof material and for water-pipes, whilst its want of conducting power for electricity is turned to account in the coating of wires for the electric telegraph.

Gutta percha is dissolved by the same substances which dissolve caoutchouc. Though it dissolves very slowly in ether, it is not affected by diluted acids and alkalies, and is employed for the manufacture of bottles in which hydrofluoric acid is kept. It liquefies at a moderately high temperature, and is afterwards decomposed, yielding products similar to those obtained from caoutchouc.

The gutta percha of commerce appears to contain only about 80 per cent. of pure gutta percha ($C_{40}H_{32}$), which is soluble in ether, the remainder consisting of two resins which may be dissolved out by boiling with alcohol, when a white crystalline resin ($C_{40}H_{32}O_4$) is deposited on cooling, leaving an amorphous resin ($C_{40}H_{32}O_2$) in solution.

Pure gutta percha, exposed to air, is gradually converted into these resinous bodies, unless light be excluded.

356. Gums.—Connected with the substances just described as being immediate products of vegetable life, are the *gums*, which, though resembling the resins in transparency and lustre, are at once distinguished from them by their solubility or softening in water, and by their insolubility in alcohol.

* A mixture of sulphur and chloride of lime is said to be sometimes employed.

'um arabic, which may be studied as the representative of this class, i exudation from certain species of acacia, and consists essentially of *ine*, which has the composition $C_{12}H_{11}O_{11}$. It dissolves readily, even old water, in large proportion, forming a viscid liquid, from which the ine is precipitated in white flakes on adding alcohol.

When arabine is boiled with diluted sulphuric acid, it is converted slowly grape-sugar ($C_{12}H_{14}O_{14}$) by assimilating the elements of three equiva- of water, a property connecting it closely with starch, which is sus- ible of a similar conversion.

ut a chemical property distinguishing the gums is their behaviour nitric acid, which furnishes *mucic acid* ($2HO . C_{12}H_8O_{14}$) and oxalic ($HO . C_2O_3$). The latter acid is also formed by the action of nitric upon starch and sugar, whilst mucic acid may be obtained by a lar process from sugar of milk and from manna sugar (mannite).

'um senegal is often used in place of gum arabic, especially by calico- ters to thicken their colours. It is darker in colour than gum arabic, also consists essentially of arabine.

'um tragacanth ($C_{12}H_{10}O_{10}$), which exudes from the *Astragalus Traga- ha*, is far less transparent than gum arabic, from which it also differs ot dissolving in water, but merely swelling up to a soft gelatinous s. This variety of gum, which is also called *mucilage*, *cerasine*, or *orine*, is found, together with arabine, in the gum which exudes the cherry, plum, almond, and apricot trees, and gives the mucila- us character to the watery decoctions prepared from certain seeds, such nseed and quince-seed, and from the root of the marsh-mallow.

Starch.

57. Starch ($C_{12}H_{10}O_{10}$) differs widely from the vegetable products just ed, in being an indispensable constituent of certain parts of plants, ossessing an organised structure, and playing a very important part in nutrition of the plant.

composition, it is seen to correspond with cellulose, which has also, ll be remembered, an organised structure; but the function of cel- e in the plant appears to be chiefly, if not entirely, a mechanical one, it forms the skeleton or framework of the plant, for which its resist- to chemical change especially adapts it; whilst it will be seen that h suffers chemical changes in the vegetable, which may be compared me measure to the digestion of the food in the animal body.

arch is manufactured chiefly from potatoes, wheat, and rice.

e solid portion of the potato consists chiefly of starch, as appears in ollowing result of analysis :—

Composition of the Potato.

Water,	75·9
Vegetable albumen,	2·3
Oily matter,	0·2
Woody fibre,	0·4
Starch,	20·2
Mineral substances,	1·0
	100·0

order to extract the starch, the potatoes are rasped to a pulp, which shed upon a sieve, under a stream of water, as long as the latter is

rendered milky by the starch suspended in it, the woody fibre bei behind upon the sieve. The milky liquid is allowed to settle, an clear water drawn off; the deposited starch is then stirred up with water, and again allowed to subside, this process being repeated as as the water is coloured, after which the starch is mixed with a quantity of water, and passed through a fine sieve to separate me cally mixed impurities; it is finally drained and dried, first, in a c of air, and afterwards by a gentle heat.

Starch cannot be extracted from wheat so easily as from potato account of the much larger proportion of other solid matters from it must be separated.

Composition of Wheat.

Water,	12·1
Vegetable albumen,	2·0
Oily matter,	1·1
Woody fibre,	1·5
Starch,	60·8
Dextrine and sugar,*	10·5
Gluten,	10·5
Mineral substances,	1·5
	100·0

To extract the starch, the coarsely-ground wheat is moistene water, and allowed to putrefy, as it easily does, in consequence of th able character of the gluten (which contains carbon, hydrogen, ni oxygen, and sulphur); the putrefying gluten excites fermentation sugar and part of the starch, producing acetic and lactic acids. acids are capable of dissolving the remainder of the gluten, whi then be washed away by water, the subsequent processes being sir those employed in the extraction of potato starch.

A far more economical and scientific method of extracting the consists in dissolving the gluten by means of a weak alkaline s which leaves the starch untouched. This process is especially ap the manufacture of starch from rice, the composition of which given :—

Composition of Rice.

Water,	5·0
Starch,	88·0
Gluten,	6·0
Woody fibre,	4·8
Sugar, Dextrine,	1·0
Oily matter,	0·1
Mineral matters,	0·1
	100·0

The whole rice is allowed to soak for twenty-four hours in w taining $\frac{1}{250}$th of its weight of caustic soda; it is then washed an into flour, which is again soaked for two or three days in a fresh solution; the starch is allowed to settle, and the alkaline liquor the gluten in solution is drawn off. To complete the purificatic tarch, it is stirred up with water, the heavier woody fibre allowe

* The existence of sugar in wheat is denied by Péligot.

d the milky liquid is run off into another vessel, where it deposits
ch.

h is usually sent into commerce in the rough prismatic fragments
ich it splits during the process of drying, and is generally coloured
the addition of a little artificial ultramarine or smalt, in order to
the yellow tint of linen. Commercial starch generally contains
8 per cent. of water.

h being possessed of an organised structure, might be expected to
external characters with the source from which it was derived;
cordingly, we find that, with the help of the microscope, it may be
ned from what plant any particular specimen of starch was pro-
a result which could not be arrived at by a chemical examination.

, powdered starch from the potato (P, fig. 271) appears under the
ope in very irregular ovoid granules, marked with concentric rings,
larger size than those from most other vegetables, the long diameter

Fig. 271.

grains being usually about $\frac{1}{300}$ inch. Wheat starch (W) exhibits
which are nearly circular, and are not marked with rings; they are
maller than those of potato starch, having a diameter of about
f an inch. The grains of rice starch (R) are angular, and still
measuring only about $\frac{1}{3000}$ of an inch in diameter. A. represents
ch granules of arrow-root.

h is quite unaffected by cold water; but if it be heated with water
nperature above 140° F., the granules swell up, burst, and yield
l-known viscid liquid used by laundresses. If this be mixed with
quantity of water, and allowed to stand, some of the imperfectly
ranules subside, but the greater part of the starch remains so inti-
mixed with the water, that it is not separated by filtration through
hough it has been shown that when the rootlets of a hyacinth are
ed in the diluted magma of starch, the water alone is taken up by
illary vessels, affording a strong presumption that the starch was
in a state of suspension in the water. If the boiled starch be eva-
to dryness, a brittle mass remains, which may again be taken up
difficulty by water.

peculiar behaviour of starch with water is closely connected with
as food. Raw starch is digested with difficulty, and often passes
ed through the bowels, but the ease with which the starch gela-
by heat is digested, is shown by the wholesomeness of sago,
and arrowroot, which consist simply of starch, and are prepared for
heating them with water to the point at which the granules burst.
w-root is the starch extracted from the root of the *Maranta arun-*
, and of some other tropical plants.

he preparation of tapioca and sago, the starch is dried at a tem-
e above 140° F., so that it loses its ordinary farinaceous appearanc
omes semi-transparent.

Sago is manufactured from the pith of certain species of palm, natives of the East Indian islands. The tree is split so as to expose the pith, which is mixed with water, and the starch having been separated from the woody fibre in the usual manner, is pressed through a perforated metallic plate, which moulds it into small cylinders; these are placed in a revolving vessel and broken into rough spherical grains, which are steamed upon a sieve, and dried.

Tapioca is obtained from the roots of the *Jatropha manihot*, a native of America. The roots are peeled and subjected to pressure, which squeezes out a juice employed by the Indians to poison their arrows, and containing a deleterious substance which has been named *jatrophine*. When the juice is allowed to stand, it deposits starch, which is well washed, pressed through a colander, and dried at 212° F.

358. *Dextrine.*—When starch is heated in an oven to about 400° F. for an hour or two, it becomes easily soluble in cold water, yielding a solution having all the properties of gum; the starch has indeed been converted into a new substance known as *dextrine* or *British gum*, which is largely used by calico-printers for thickening their colours, and is substituted for ordinary gum in many other applications. There is a current anecdote which attributes the discovery of dextrine to a conflagration at a starch-factory, where the work-people, who assisted in quenching the fire, observed the gummy properties of the water which had been thrown over the torrefied starch. In toasting bread, a portion of the starch is converted into dextrine, which is dissolved by the water in the preparation of toast and water.

It is very remarkable that the composition of dextrine ($C_{12}H_{10}O_{10}$) is precisely that of starch; they are *isomeric* bodies, so that the difference in their properties must be ascribed to a difference in the arrangement of their component particles; the name of dextrine was conferred upon this gummy substance on account of the power possessed by its solution of causing a right-handed rotation in a ray of polarised light. When oxidised by nitric acid, dextrine, like starch, is converted into oxalic acid, a circumstance distinguishing it from ordinary gum, which furnishes mucic acid when acted upon by nitric acid.

Dextrine is usually prepared on the large scale by moistening 10 parts of starch with 3 parts of water acidulated with $\frac{1}{10}$th of nitric acid; the mixture is allowed to dry, and spread upon trays in an oven, where it is heated for an hour or so to 240° F. The nitric acid thus allows the starch to be converted into dextrine at a temperature which would be quite inadequate to effect the transformation of starch alone.

This power of accelerating the conversion of starch into dextrine is shared by all acids. Hence if starch be boiled with water, and the viscid liquid so obtained be mixed with an acid, and again boiled, it gradually becomes thinner, and is eventually converted into dextrine. The change is very readily effected by boiling the starch solution with a few drops of sulphuric acid, and the gradual conversion of the starch may be traced by means of an aqueous solution of iodine. On adding this solution to a portion of the (cold) solution of starch, it produces the usual dark blue colour; but on adding it, at intervals, to portions of the acidulated and boiled liquid, taken away and cooled for the purpose, the blue colour will be replaced by a peculiar vinous purple tint which iodine imparts to solutions of dextrine.

The solution of iodine is much used in proximate organic analysis as a test for starch, and it is necessary to bear in mind that the blue colour is bleached by alkalies (which take up the iodine) and by heat, though, in the latter case, it may be restored by cooling the liquid. The blue colour does not appear to be due to the formation of any definite chemical compound with the starch, but rather to a mechanical adhesion of very finely divided iodine to the particles of starch. The sensitiveness of starch to the action of *free* iodine has given rise to its application in the preparation of paper for the prevention of forgery in bankers' cheques, &c. If paper be impregnated with a mixture of iodide of potassium and starch, which is perfectly white, it will acquire an intense blue colour on the application of any of the bleaching agents (chlorine, hypochlorous acid, chlorides of lime and soda), generally used for removing ink, as these liberate the iodine, which immediately blues the starch.

If the ebullition of the dextrine in contact with the sulphuric acid be continued, the solution entirely loses its property of being coloured by iodine, and acquires a sweet taste, the dextrine having been converted into *glucose* or *grape-sugar* ($C_{12}H_{14}O_{14}$) by assimilating the elements of four equivalents of water*—

$$\underset{\text{Dextrine.}}{C_{12}H_{10}O_{10}} + 4HO = \underset{\text{Grape-sugar.}}{C_{12}H_{14}O_{14}}.$$

359. *Germination of seeds—Malting.*—This tendency of starch to combine with the elements of water and pass into grape-sugar, will be found of immense importance in the chemistry of vegetation, as well as in that of food. It is, indeed, the chief chemical change concerned in the development of living from inanimate matter, being one of the first processes involved in the germination of a seed—the first step in the production of vegetables, which must precede the animals whose food they compose.

The components of all seeds are similar to those of wheat, which have been enumerated above; and if they be perfectly dried immediately after their removal from the parent plant, they may be preserved for a great length of time unchanged, and without losing the power of germinating under favourable circumstances. The essential conditions of germination are the presence of air and moisture, and a certain temperature, which varies with the nature of the seed. These conditions being fulfilled, the seed absorbs oxygen from the air, and evolves carbonic acid, produced by the combination of the oxygen with the carbon of one or more of the most alterable constituents of the seed, such as the vegetable albumen or the gluten. This process of oxidation is attended with evolution of heat, which serves to maintain the seed at the degree of warmth most favourable to germination. The component particles of the albumen or gluten having been set in motion by the action of the atmospheric oxygen, induce a movement or chemical change in the starch with which they are in contact, causing it to pass into dextrine and grape-sugar, which, unlike the starch, being perfectly soluble in water, are capable of affording to the developing shoot, the carbon, hydrogen, and oxygen which it requires for the increase of its frame. The production of grape-sugar and of dextrine in germination is

* There is some reason to believe that the formation of grape-sugar from starch results from a change similar to that by which it is obtained from salicine and other glucosides. Thus—

$$\underset{\text{2 eqs. starch.}}{C_{24}H_{20}O_{20}} + 4HO = \underset{\text{Dextrine.}}{C_{12}H_{10}O_{10}} + \underset{\text{Glucose.}}{C_{12}H_{14}O_{14}}$$

well illustrated by the sweet gummy character of the bread made from *sprouted* wheat, and is turned to practical account in the process of malting.

During the germination of all seeds, there is formed, apparently by the oxidation of one of the more alterable constituents, a peculiar substance containing carbon, hydrogen, nitrogen, and oxygen, which has never yet been obtained from any other source, and is characterised by its remarkable property of inducing the conversion of starch into dextrine and grape sugar.

This substance has been termed *diastase* (διάστᾶσις, *dissension; metaph. fermentation*), but has never yet been obtained in a state of sufficient purity to enable its formula to be satisfactorily determined. It may be extracted, however, from malt, by grinding it, and mixing it with half its weight of warm water, which dissolves the diastase; the solution squeezed out of the malt is heated to about 170° F., filtered from any coagulated albumen, and mixed with absolute alcohol, which precipitates the diastase in white flakes. One part of diastase dissolved in water is capable of inducing the conversion of 2000 parts of starch into dextrine and grape-sugar, the diastase itself being exhausted in the process. A temperature of about 150° F. is most favourable to the action of diastase, which may be arrested entirely by raising the liquid to the boiling point.

The great importance of diastase in the arts of the brewer and distiller is at once apparent. In the process of *malting* barley, the grain is soaked in water, and afterwards spread out in thin layers upon the floor of a dark room (thus imitating the natural condition under which the seed germinates), which is maintained as nearly as possible at a constant and moderate temperature (between 55° and 62° F.); spring and autumn are, therefore, more favourable to malting than summer and winter. It soon evolves heat, and the grains begin to swell; in the course of twenty-four hours the germination commences, and the *radicle* makes its first appearance as a whitish protuberance; the grain is turned two or three times a-day, in order to equalise the temperature. In about a fortnight, the radicle has grown to about half an inch, by which time a sufficient quantity of diastase has been formed. In order to prevent the germination from proceeding further, the grain is killed by drying it at a temperature of 90° F. on perforated metallic plates, where it is afterwards heated to about 140° F., so as to render it brittle, after which it is sifted in order to separate the radicle, which is now easily broken off. This radicle is found to contain as much as $\frac{1}{7}$th of the total quantity of the nitrogen present in the barley, so that the *malt dust*, as the siftings are called, forms a valuable manure.

100 parts of barley generally yield about 80 parts of malt, but a part of the loss is due to water present in the barley, so that 100 parts of dry barley yield 90 parts of malt, and 4 parts of malt dust, the difference, viz., 6 parts, representing the weight of the carbon converted into carbonic acid, of the hydrogen (if any) converted into water during the germination, and of soluble matters removed from the barley in steeping. Malt contains about $\frac{1}{800}$th of its weight of diastase, far more than enough to ensure the conversion of the whole of its starch into sugar.

The following table* illustrates the change in composition suffered by barley during the process of malting, leaving the moisture out of consideration:—

* Lawes; Report on the Relative Values of Unmalted and Malted Barley as Food for Stock. 1866.

	Barley.	After steeping.	14½ days on floor.	Malt after sifting.	Malt Dust.
. . . . .	2·56	1·56	12·14	11·01	11·35
. . . . . }	80·42	81·12	70·09	72·03	43·68
re, ...	4·69	5·22	5·03	4·84	9·67
is matter, .	9·83	9·83	10·39	9·95	26·90
atter, . . .	2·50	2·27	2·35	2·17	8·40
	100·00	100·00	100·00	100·00	100·00

ewing.—In order to prepare beer, the brewer *mashes* the lt with water at about 180° F. for some hours, when the dias- s the conversion, into dextrine and sugar, of the greater part of which has not been so changed during the germination, and ready to be drawn off for conversion into beer.

issolved portion of the malt, or *brewers' grains*, still contains ble quantity of gluten, and is employed for feeding pigs.

lt contains far more diastase than is necessary to convert its sugar, is shown by adding a little infusion of malt to the tion of starch, and maintaining it at about 150° F. for a few n the mixture will have become far more fluid, and will no oloured blue by solution of iodine. In distilleries, advantage f the excess of diastase in malt, by adding 3 or 4 parts of grain to it, when the whole of the starch in this latter is also into dextrine and sugar, and the labour and expense of malting led.

t obtained by infusing malt in water contains not only grape- rine, and diastase, but a considerable quantity of nitrogenised med from the gluten of the barley. Before subjecting it to n, it is boiled with a quantity of hops, usually amounting to of the weight of the malt employed, which is found to prevent, easure, the tendency of the beer to become sour in consequence ersion of the alcohol into acetic acid.

contains about 10 per cent. of an aromatic yellow powder, *line*, which appears to be the active portion, and which con- tile oil of peculiar odour, together with a very bitter substance.

ped wort is run off into a vat, where it is allowed to deposit olved portion of the hops, and the clear liquor is drawn off into olers, where its temperature is lowered as rapidly as possible to F., the cooling being usually hastened by cold water circulating pes which traverse the coolers. If the wort be cooled too nitrogenised matter which it contains undergoes an alteration on of the air, in consequence of which the beer is very liable acid.

t is now transferred to the *fermenting tun*, where it is made to the addition of yeast, usually in the proportion of $\frac{1}{100}$th of

a minute fungoid vegetable, which grows in solutions contain- together with some nitrogenised substance (*e.g.*, a salt of *and the salts* (phosphates of potash, soda, lime, and magnesia),

which are essential constituents of its cells. It is only recently that the conditions under which the yeast plant grows have been ascertained, and the seeds or germs from which it originates have hitherto eluded detection, though it may be remarked that in this respect it only resembles some of the lower mosses, the vegetable character of which has never been called in question.

If a little white of egg, cheese, or a piece of flesh (all of which contain carbon, hydrogen, nitrogen, oxygen, and phosphates), be placed in a solution of sugar, and allowed to undergo decomposition, a grey scum forms upon the liquid, which is seen under the microscope to consist of irregularly oval cells, the growth of which may be watched under the microscope in a little of the liquid from which they were obtained, when they will be found to multiply rapidly by the production of new cells on all sides of them (fig. 272). The same cells will be developed very rapidly in the sweet wort of malt, allowed to undergo decomposition between 60° and 70° F.

Fig. 272.

These cells contain a substance somewhat resembling albumen, enclosed in a thin membrane, the composition of which is similar to that of cellulose. They also contain a peculiar nitrogenised body resembling diastase, and capable of inducing the conversion of cane-sugar ($C_{12}H_{11}O_{11}$) into grape-sugar ($C_{12}H_{14}O_{14}$). Accordingly, when yeast is added to a solution of cane-sugar, the liquid is found to increase in specific gravity (a solution of cane-sugar having a lower density than one containing an equivalent quantity of grape-sugar), previously to the commencement of fermentation, and the application of tests readily proves the presence of grape-sugar in the solution.

The grape-sugar then undergoes the decomposition known as *alcoholic fermentation*, which results in the production of alcohol, carbonic acid, lactic acid, succinic acid, glycerine, and a peculiar brown soluble matter, together with other substances, the true nature of which is yet undetermined. The fermentation is attended with a considerable elevation of temperature.

Taking into consideration only the alcohol and carbonic acid, which are the chief products, their formation from grape-sugar may be represented by the equation—

$$\underset{\text{Grape-sugar.}}{C_{12}H_{14}O_{14}} = \underset{\text{Alcohol.}}{2C_4H_6O_2} + 4CO_2 + 2HO.$$

During the fermentation, the yeast cells are gradually broken up, so that a given quantity of yeast is capable of fermenting only a limited quantity of sugar. On an average, a quantity of yeast containing between two and three parts of solid matter is required to complete the fermentation of 100 parts of sugar. The solution remaining after the fermentation is found to contain salts of ammonia, which have been formed at the expense of the nitrogen of the yeast.

If the liquid in which the yeast excites fermentation contain nitrogenised matters and phosphates, the yeast plant grows, and its quantity increases; thus in the sweet wort from malt, the yeast is nourished

gluten and by the phosphates, so that it increases to six or its original weight.

be heated to the boiling point of water, the plant is killed, as pected, and loses its power of inducing alcoholic fermentation; be dried at a low temperature, or by pressure, without losing ng power, and *dried yeast* is an article of commerce.

ll not cause fermentation in a solution containing more than f its weight of sugar, and the fermentation is arrested when amounts to one-fifth of the weight of the liquid, so that the fermented liquors could never exceed 20 per cent of alcohol. tation is also arrested by the mineral acids, and by many of ices to which antiseptic properties are commonly attributed, mon salt, kreasote, corrosive sublimate, sulphurous acid, tur-

rmentation of beer, the yeast is carried up to the surface by the e due to the escape of the carbonic acid, and is eventually n order to be employed for the fermentation of fresh quantities

ne fermentation has proceeded to the required extent, the beer r consumption.

e seen that the chief constituents of beer are the alcohol, the l matter derived from the gluten of the barley, and not con- ne growth of the yeast, the unaltered sugar and dextrine, the ellow colouring matter formed during the fermentation, the l and bitter principle of the hop.

contains acetic acid (formed by the oxidation of the alcohol, e carbonic acid, which gives its sparkling character, together ctic and succinic acids and glycerine, formed as secondary pro- fermentation, and ammoniacal salts derived from the yeast. mineral substances from the barley are also present, *minus* ates abstracted by the yeast.

portions of the constituents of course vary greatly, as will be he following examples :—

age of—	Allsopp's Ale.	Bass's Ale.	Strong Ale.	Whitbread's Porter.	Whitbread's Stout.
. . . .	6·00	7·00	8·65	4·20	6·00
. . . .	0·20	0·18	0·12	0·19	0·18
other solid	5·00	4·80	6·60	5·40	6·38

k colour of porter and stout is caused by the addition of a *high-dried malt* which has been exposed to so high a tempera- kiln as to convert a portion of its sugar into a dark brown stance called caramel. It is said that alum and sulphate of so added to porter and stout to cause them to froth strongly. r aroma of beer is probably due to the presence of a minute some fragrant ether, produced during the fermentation.

cases, when the operation of brewing has been badly con- beer becomes *ropy*, or undergoes the *viscous fermentation*. In e sugar suffers a peculiar transformation, resulting in the pro- a mucilaginous substance resembling gum in its composition. *may be induced* in sugar by yeast which has been boiled, or

by water in which flour or rice has been steeped. White wines sionally become ropy from a similar cause, but red wines are not li this change, apparently because the tannin which they contain has pitated in an insoluble form the ferment which induces it. During viscous fermentation a part of the sugar is often converted into m $(C_{12}H_{14}O_{12})$.

361. ACETIFICATION—MANUFACTURE OF VINEGAR.—Beer whi become sour is often said to have undergone the *acetous fermentation* this is not strictly correct, the change being more similar to decay it is one in which the oxygen of the air directly takes part. The of sour beer is caused by the acetic acid $(C_4H_4O_4)$ formed by the ac atmospheric oxygen upon the alcohol, according to the equation—

$$\underset{\text{Alcohol.}}{C_4H_6O_2} + O_4 = \underset{\text{Acetic acid.}}{C_4H_4O_4} + 2HO.$$

Pure alcohol may be exposed to the air, either alone or when mix water, for any period, without suffering oxidation; but when in with certain changeable organic substances, the alcohol undergoes tion, and is converted into acetic acid. It is upon this circumstan the different methods of producing vinegar are based.

The most direct application of this principle is made in the *quick vinegar process* in use in continental countries where al free of duty. Alcohol of about 80 per cent. is mixed with 6 water, and with about $\frac{1}{100}$ of yeast, or some other altera stance containing nitrogen. T ture is heated to about 80° caused to trickle slowly from cord fixed in a perforated she quantity of wood shavings* p soaked in vinegar, which materially to assist the acet and packed in a tall cask (fi in which holes have been d order to allow the entrance of oxidation of the alcohol soon temperature to about 100° F occasions a free circulation among the shavings. The m

Fig. 273.

passed three or four times through the cask, and in about 36 h conversion into vinegar is completed. The oxidation of the a this process is found to be arrested by the presence of essential creasote, and similar antiseptic substances.

The necessity of affording a full supply of atmospheric air appreciated until Liebig had proved the existence of an intermedi in the process, consisting in a partial oxidation of the alcohol it became converted into *aldehyde* $(C_4H_4O_2)$, an extremely volat (boiling at 70° F.), which was lost in the form of vapour, thu diminishing the proportion of vinegar obtained—

$$\underset{\text{Alcohol.}}{C_4H_6O_2} + O_2 = \underset{\text{Aldehyde.}}{C_4H_4O_2} + 2HO.$$

* These shavings appear to favour the process by serving as points of attach microscopic vegetable, which encourages the oxidation of the alcohol.

fficient quantity of atmospheric air be supplied, the production of
le is entirely avoided.
te wine vinegar is prepared in France from light wines by a process
h longer duration. A little boiling vinegar is poured into a cask,
y open at the top, together with four or five gallons of white wine
has been allowed to trickle over wood shavings. In a few days,
which the temperature is maintained at about 80°, a fresh quantity
is poured in, and in the course of a fortnight half the vinegar con-
in the cask is drawn off, and replaced by a fresh portion of wine.
way an occasional renewal of the air in the upper part of the cask
ided for. The acetification is found to proceed more rapidly in old
han in new ones, which is attributed to the presence of a peculiar
a deposited upon the sides of the former, and styled *mother of*
. It is probably for a similar reason that the acetification is pro-
by the addition of ready-made vinegar at the commencement of the
.
his country vinegar is chiefly prepared from malt, the infusion of
is allowed to undergo the alcoholic and acetous fermentation.
gar contains on an average about 5 per cent. of acetic acid, together
nall quantities of vegetable and mineral substances, varying with
rce from which it was obtained. Its pleasant aroma is due to the
e of some *acetic ether* ($C_4H_5O \cdot C_4H_3O_3$) formed during its manu-
. The vinegar of commerce is allowed to be mixed with $\frac{1}{1000}$th
weight of sulphuric acid in order to prevent it from becoming
.

Bread.

The chemistry of fermentation is intimately connected with the ordi-
ocess of bread-making. It will be remembered that wheaten flour
) consists, essentially, of starch and gluten, with a little dextrine
gar. On mixing the flour with a little water, it yields a *dough*, the
y of which is due to the gluten present in the flour. If this dough
up in a piece of fine muslin, and kneaded under a stream of water,
rch will be suspended in the water, and will pass through the
, whilst the gluten will remain as a very tough elastic mass, which
y putrefies if exposed to the air in a moist state, and dries up to a
horny mass at the temperature of boiling water.
nalysis, gluten is found to contain carbon, hydrogen, nitrogen, and
, in proportions which may be represented by the empirical formula
N_3O_n, though it cannot be regarded as a single independent sub-
but as a mixture of three substances very closely allied in compo-

n gluten is boiled with alcohol, one portion refuses to dissolve, and
n named *vegetable fibrine*, from its resemblance to the substance
the muscles of animals. When the solution in alcohol is allowed
it deposits a white flocculent matter, very similar to the *caseine*
composes the curd of milk. On adding water to the cold alcoholic
, a third substance (*glutine*) is separated, which much resembles
umen found so abundantly in the blood.
presence in gluten of three substances, similar to the three principal
ents of the animal body, leads us to form a high opinion of

value as a nutritive compound. But gluten itself, separated from the flour by the process above described, would be found very difficult of digestion, on account of its resistance to the solvent action of the fluids in the stomach; indeed, the dough composed of flour and water is proverbially indigestible, even when baked. In order to render it fit for food, it must be rendered spongy or porous, so as to expose a larger surface to the action of the digesting fluids of the body; the most direct method of effecting this is the one adopted in the manufacture of the *aerated bread*, and consists in mixing the flour with water which has been highly charged, under pressure, with carbonic acid gas; the mixing having been effected in a strong closed iron vessel, an aperture in the lower part of this is opened, when the pressure of the accumulated gas forces the dough out into the air, and the gas which had been imprisoned in the dough expands, conferring great porosity and sponginess upon the mass in its attempt to escape. In another process for preparing *unfermented bread*, the flour is mixed with a little bi-carbonate of soda, and is then made into a dough with water acidulated with hydrochloric acid; the latter decomposing the bi-carbonate of soda, liberates its carbonic acid, which renders the bread porous. The chloride of sodium formed at the same time remains in the bread. In the preparation of cakes and pastry, the same object is sometimes attained by adding carbonate of ammonia to the dough. When heat is applied, in the baking, the salt is converted into vapour which distends the dough.

In the common process of bread-making, however, the carbonic acid destined to confer sponginess upon the dough is evolved by the fermentation of the sugar contained in the flour; the latter having been kneaded with the proper proportion (usually about half its weight) of water, a little yeast and salt are added, and the mixture is allowed to stand at a temperature of about 70° F. for some hours. The dough swells or *rises* considerably, in consequence of the escape of carbonic acid, the sugar being decomposed into that gas and alcohol, as in ordinary fermentation. The spongy dough is then baked in an oven, heated to about 500° F., when a portion of the water and the whole of the alcohol are expelled, the carbonic acid being also much expanded by the heat, and the porosity of the bread increased. The granules of starch are much altered by the heat, and become far more digestible. Although the temperature of the inside of the loaf does not exceed 212° F. the outer portion becomes dry and hard, the hottest part being even torrefied or scorched into crust.

Occasionally, instead of yeast, *leaven* is employed, in order to ferment the sugar, leaven being dough which has been left in a warm place until decomposition has commenced.

The passage of new into stale bread does not depend, as was formerly supposed, upon the drying of the bread consequent upon its exposure to air, but is a true molecular transformation which takes place equally well in an air-tight vessel, and without any loss of weight. It is well known that when a thick slice of stale bread is toasted, which *dries* it still further, the crumb again becomes soft and spongy as in new bread; and if a stale loaf be again placed in the oven, it is entirely reconverted into new bread.

Wheaten flour is particularly well fitted for the preparation of bread on account of the great tenacity of its gluten. Next to wheat in this respect stands rye, whilst the other cereals contain a gluten so deficient in tenacity that it is impossible to convert them into good bread.

Even in wheaten flour the tenacity of the gluten is liable to variation, and in order to obtain good bread from a flour the gluten of which is inferior in this respect, it is customary to employ a minute proportion of alum. This addition being considered unwholesome by some persons, it would be better to substitute lime-water, which has been found by Liebig to have a similar effect. Sulphate of copper improves in a very striking manner the quality of the bread prepared from inferior flour, but this salt is far more objectionable than alum.

The Sugars.

363. The conversion of starch into grape-sugar, when heated in contact with diluted acids (p. 487), is taken advantage of for the preparation of this variety of sugar on the large scale. For this purpose, water acidulated with $\frac{1}{100}$th of sulphuric acid is heated to ebullition, and a hot mixture of starch and water allowed to flow gradually into it, so as not to reduce its temperature below the boiling point. The mixture is kept boiling for half-an-hour, after which chalk is added in small portions at a time to neutralise the sulphuric acid, and the sulphate of lime having been allowed to subside, the clear syrup is drawn off, and evaporated to the crystallising point.

The grape-sugar or *glucose* thus manufactured cannot be employed as a substitute for the sugar extracted from the sugar-cane, on account of its greatly inferior sweetening power, which is less than half that possessed by cane-sugar. It is, moreover, far less soluble in water, 1 part of grape-sugar requiring $1\frac{1}{2}$ part of water to dissolve it, whilst cane-sugar requires only $\frac{1}{3}$ part. Grape-sugar is employed, however, for the adulteration of cane-sugar; and the very crystalline, nearly white samples of *moist* sugar met with in the shops, are usually largely adulterated in this way. The fraud is easily detected by boiling a portion of the sample with a little solution of potash, when the grape-sugar is decomposed, and colours the liquid intensely brown, pure cane-sugar giving very little brown colour unless boiled for a long time. A more delicate mode of detection consists in adding to a solution of the sugar a few drops of solution of sulphate of copper, and enough solution of potash to form an intensely blue liquid. The oxide of copper is not precipitated in the presence of either of the sugars; but if the blue liquid be very gently heated, a red precipitate of suboxide of copper will separate if grape-sugar be present, whilst with pure cane-sugar the precipitation does not take place unless the solution is boiled.

Even cellulose is transformed into dextrine and grape-sugar under the influence of sulphuric acid. If linen, calico, cotton-wool, or paper be dried, and gradually moistened with $1\frac{1}{2}$ part of concentrated sulphuric acid, avoiding elevation of temperature, it is converted in the course of a few hours into a gummy mass which dissolves in water, and is very similar to dextrine. When the cellulose has been left in contact with the acid for a day or two, it should be dissolved in a large quantity of water, and boiled for 8 or 10 hours in order to effect the conversion into sugar; the acid may then be neutralised with chalk, the solution filtered from the sulphate of lime, and evaporated, when it furnishes a crystalline mass of grape-sugar.

Closely connected with the conversion of cellulose into dextrine by

contact with strong sulphuric acid, is that very remarkable change of paper into *vegetable parchment*. If dry white blotting-paper be drawn through a cooled mixture of the strongest oil of vitriol with half its bulk of water, and be then thoroughly washed in a large volume of water, it becomes five times as strong as before, and has $\frac{3}{4}$ths of the strength of ordinary animal parchment. The parchment paper, when dry, is found to have suffered no alteration in weight, and analysis shows its composition to be unchanged. This remarkable increase in strength must, therefore, be referred to a molecular alteration. The paper is also found to have become almost waterproof, and presents a somewhat translucent appearance like paper which has been slightly oiled. It receives many useful applications, for luggage labels which are not easily torn or removed by rain, and as a substitute for animal membrane in tying over preserves, &c.

This susceptibility of conversion into grape-sugar possessed by starch and cellulose, affords a very important clue in tracing the changes which take place in living vegetables. It has been already seen (p. 487) that during the germination of seeds, their starch is converted into sugar, in order that it may be carried in a soluble form to the extending limbs of the vegetable frame; but it would appear that in these parts, where a deposition of cellulose is required, the sugar ($C_{12}H_{14}O_{14}$) is reconverted into that substance ($C_{12}H_{10}O_{10}$). In the ripening of the fruit, however, the ligneous matter and the starch seem to be again converted into sugar, under the influence of the vegetable acids which unripe fruits contain.

Strictly speaking, the sugar contained in ripe fruits and in new honey is not grape-sugar ($C_{12}H_{14}O_{14}$), but a distinct variety of sugar known as *fruit sugar* or *fructose*, and having the composition ($C_{12}H_{12}O_{12}$). This sugar has also been designated, in reference to its characteristic feature, *uncrystallisable sugar*, and its production seems to constitute an intermediate stage in the transition of starch, cellulose, and cane-sugar into grape-sugar. Hence it is found that if the ebullition with diluted sulphuric acid be arrested as soon as the liquid becomes sweet, no crystals can be obtained, but on further ebullition, the fructose is converted into crystallisable glucose. When honey is kept for some time, the fructose gradually becomes converted into a crystalline mass of glucose. The same change is seen to take place in raisins, which contain granules of glucose, though the fresh grapes contain only fructose.

The uncrystallisable sugar forms the chief ingredient of *molasses* and *treacle*, for although the fresh juice of the sugar-cane contains no fructose the treatment to which it is subjected in the extraction of the sugar occasions a copious formation of the uncrystallisable sugar at the expense of the cane-sugar. The simple ebullition of a solution of cane-sugar for a considerable period is said to convert a portion of it into fructose, and if a minute quantity of any uncombined acid be present, the change takes place very rapidly.

364. *Extraction of cane-sugar.*—In the extraction of sugar from the sugar-cane, the latter is cut before the period of flowering, when, as might be expected, this soluble nutriment of the plant is most abundant. For a similar reason, the canes are cut off close to the ground, since in the higher joints of the cane much of the sugar has already been consumed for their development.

ıen of sugar-cane from Martinique was found to contain :—

Juice, ...	90·1
Woody fibre, . .	9·9
	100·0

ıoretically, 100 parts of cane should yield as much as 90 parts The canes are crushed between iron cylinders, which express, ıest arrangements, only 65 parts of juice from 100 of cane. It und possible to increase the yield by steaming the canes before them to a final pressure. The juice thus expressed contains ır cent. of sugar, together with the usual components of the ts, such as vegetable acids, albumen, salts, &c.

opical climate in which the extraction is conducted, the albu- juice speedily alters when exposed to the air, and excites n in the sugar, by which a considerable quantity would be ıe fresh juice were heated to coagulate the albumen, the free ıed in it would change a portion of the sugar into the uncrys- ıriety. To avoid this, the juice is mixed with $\frac{1}{800}$th part of , and is then heated to 140° F. in large flat copper pans. The albumen rises to the surface of the heavy syrup, and forms a , which is taken off, and the clear syrup is evaporated till it is ıgh to crystallise, when it is run off into shallow wooden vats, l to cool for 24 hours. When briskly stirred, it congeals to a nass of crystals, which are allowed to drain for three weeks in perforated bottoms. The raw sugar thus obtained, after dry- ıun, is sent into commerce, the drainings being styled molasses The weight of raw sugar seldom exceeds $\frac{1}{10}$th of the juice, ıut half the quantity which the juice is known to contain, ler having been converted into uncrystallisable sugar during of extraction. The loss is found to be materially dimi- the use of *vacuum pans*, in which the evaporation of the nducted under diminished pressure, and therefore at a lower . Greater economy is also introduced into the manufacture by he crushed canes as fuel for the evaporating fires, and by re- r ashes to the land as food for ensuing crops. The skimmings ied juice are also advantageously used as manure.

sugar obtained by the process just described contains about . of pure cane-sugar, the remainder consisting of water, un- le sugar, colouring matter, and various salts and other foreign derived from the cane-juice.

rdinary process of *sugar-refining*, two or three parts of raw ssolved in one part of water containing a little lime in solution, with three or four parts of ground bone-black for every hundred small quantity of serum of bullock's blood is also generally his mixture is heated by the passage of steam through it, lbumen of the serum is coagulated, and rises to the surface in a scum which entangles the floating impurities as well as the and leaves the syrup much lighter in colour, a considerable colouring matter having been removed by the charcoal (p. 59). p is then filtered through a thick layer of coarsely powdered and is thus rendered perfectly colourless and ready for evapora- *is conducted in* a boiler with double sides, so that it may be

heated by steam admitted between the two, and furnished with a dome from which the air may be exhausted in order to allow the evaporation to be conducted at a lower temperature, as well as out of contact with the atmospheric oxygen, so as to diminish as far as possible the production of uncrystallisable sugar. The boiling down of the syrup, which would require a temperature of 230° F. at the ordinary pressure, may thus be conducted at 160° F. When sufficiently evaporated,* the syrup is transferred to a heated vat, where it is stirred until a confused crystallisation commences, and is then drawn off into inverted sugar-loaf moulds of iron or earthenware, and allowed to crystallise during about 20 hours. The crystalline mass is then allowed to drain by the withdrawal of a plug at the apex of the inverted cone, and is washed with a little pure syrup to remove adhering colouring matter, after which the loaf is dried in an oven and finished by turning in a lathe.

The operation of washing with syrup is often referred to as *claying*, being sometimes effected by placing some powdered sugar upon the base of each loaf, and over this a cream of pure pipe-clay, the water draining from which dissolves the powdered sugar, and the syrup thus formed washes the loaf. The object of the clay appears to be simply to allow the water to flow gradually through the sugar.

The process of refining is sometimes shortened by washing the raw sugar with strong syrup, so as to remove the bulk of the impurities at the commencement, and a very ingenious method, known as the *centrifugal process*, has been devised for separating the syrup from the sugar thus washed. The pasty mixture of sugar and syrup is introduced into a cylinder of strong close metallic gauze, which is rapidly turned upon its axis, when the liquid syrup of course flies off through the apertures of the gauze, and is collected by a box surrounding the cylinder. A fresh quantity of syrup is then introduced, and separated in the same manner, so that the washing may be rapidly carried as far as may be deemed expedient.

365. During the wars of Napoleon, when the importation of sugar into France was suspended, this substance was extracted from the beet-root, and this process still forms a very important branch of French industry.

The white beet only is employed, on account of the difficulty of separating the colouring matter existing in the juice of the red variety. The juice contains about ten per cent of cane-sugar, half of which only is usually obtained in the crystallised state. The process adopted for extracting it does not differ in principle from that applied to the juice of the sugar-cane.

Cane-sugar is also extracted in the United States from the sap of the sugar-maple, which is collected, usually in the spring, from deep incisions through the bark, into each of which a pipe of reed or elder is inserted to conduct the juice into pans placed for its reception, whence it is removed before it has had time to become changed by fermentation. The juice is evaporated rapidly, and the raw crystalline mass sold without further refining. On an average, each tree furnishes about six pounds of sugar during the season.

Sugar-candy consists simply of large rhomboidal prismatic crystals of sugar deposited upon strings stretched across crystallising troughs, in which a strong syrup is slowly evaporated at about 170° F.

* The state of concentration of the syrup is known by the degree of viscidity which it exhibits between the finger and thumb, by the length of the thread to which it may be drawn, and by the mode in which this curls after breaking.

Barley-sugar is prepared by evaporating the syrup beyond the crystallising point, till it solidifies on cooling, to a vitreous mass, which is poured on a cold surface and manipulated to the requisite forms. When kept for some time, the transparent barley-sugar becomes crystalline and opaque.

Caramel ($C_{12}H_9O_9$) is a dark-brown substance produced by the action of a temperature of about 400° F. upon melted sugar. It is very soluble in water, and gives an intensely brown liquid, for which reason it is employed in colouring sauces, gravies, brandy, wines, &c.

356. *Chemical properties of the sugars.*—Although cane and grape-sugar appear to be essentially indifferent substances, they are remarkably prone to form combinations with many basic metallic oxides. Thus a solution of cane-sugar is capable of dissolving a large quantity of lime, forming a compound ($CaO . C_{12}H_{11}O_{11}$) which is much more soluble in cold than in hot water, so that on boiling the transparent solution it becomes perfectly opaque, but resumes its transparency on cooling.

On boiling the hydrated oxide of lead with a solution of sugar, it is dissolved, but as the solution cools, a white powder is deposited, which has the composition $2PbO . C_{12}H_9O_9 + HO$, the equivalent of water being expelled at a temperature of 212°. The composition of this compound would lead to the belief that cane-sugar contains two equivalents of constitutional water, and that its formula should be written $C_{12}H_9O_9 . 2HO$. By carefully heating cane-sugar, the compound, $C_{12}H_{10}O_{10}$, *saccharide*, has been obtained, and if this be further heated it yields $C_{12}H_9O_9$, *caramel*. When a solution containing 1 part of salt and 4 parts of sugar is allowed to evaporate spontaneously, it deposits a deliquescent compound consisting NaCl. $2(C_{12}H_9O_9)$. 3HO.

Many metallic oxides form compounds with sugar, which are readily soluble in alkaline liquids, so that the addition of sugar to solutions of the oxides of copper and iron prevents the precipitation of these oxides by the alkalies.

Grape-sugar also combines with many bases. The compounds which it forms with the alkalies are very unstable, and their solutions, which are at first alkaline, soon become neutral in consequence of the conversion of the grape-sugar into *glucic acid* ($3HO . C_{24}H_{18}O_{15}$) by the loss of the elements of water.

By saturating a solution of grape-sugar with common salt, a liquid is obtained which deposits well-defined crystals, having the composition $2(C_{12}H_{13}O_{13}) . NaCl . 2HO$. When dried at 212° it becomes $2(C_{12}H_{12}O_{12}) . NaCl$. The true formula of grape-sugar is obviously $C_{12}H_{12}O_{12} . 2HO$, for if it be dissolved in hot strong alcohol (which dissolves far more grape-sugar than cane-sugar) it crystallises on cooling, in prisms, which have the formula $C_{12}H_{12}O_{12}$. Two equivalents of water may also be expelled from ordinary grape-sugar at 212° F.

The action of sulphuric acid upon cane and grape-sugar is very different; the former is carbonised and completely decomposed, whilst the latter combines with the sulphuric acid to form *sulphosaccharic acid*, which yields soluble salts with lime and baryta.*

The optical properties of solutions of the sugars are now often turned to account for their identification, and even for the determination of their quantities. Grape-sugar and cane-sugar both rotate the plane of polarisation of a ray from left to right, cane-sugar having rather a more powerful action, but the uncrystallisable fruit-sugar rotates the plane in the opposite direction, from right to left. If a solution of cane-sugar, possessing the rotatory power from left to right be heated with hydrochloric acid, it acquires the power of rotating the plane of polarisation from right to left, in consequence of the conversion into uncrystallisable sugar.

Starch-sugar exhibits three different modes of action upon polarised light, for a solution which has been kept some hours rotates the plane of polarisation only half as much as the freshly made solution; and if the sugar prepared from malt be dissolved in water, the solution has thrice the rotatory power which it possesses after being kept, and its rotatory power is one-third higher than that of the freshly dissolved starch-sugar. All these may be reduced at once to the lowest rotatory power by heating them nearly to ebullition and allowing them to cool.

* *Ethyle-glucose*, a bitter, fragrant oily substance, has been obtained by acting upon grape-sugar with bromide of ethyle and potash; it may be represented by the formula $H_5(C_4H_5)_2O_{10}$.

367. *Mannite* ($C_{12}H_{14}O_{12}$), the sweet principle of manna (the concrete juice of the *Fraxinus ornus*), has already been noticed as one of the products of that peculiar kind of fermentation known as the *viscous*, to which beet-root juice is especially liable. It is also found in certain mushrooms, in sea weeds, celery, asparagus, and onions. By treating manna with hot alcohol, and allowing the filtered solution to cool, the mannite may be obtained in beautiful prismatic crystals, which have a sweet taste and dissolve readily in water. Mannite differs widely from cane and grape-sugar in not fermenting when placed in contact with yeast; and this circumstance, taken in conjunction with its composition, which differs so much from that of other members of the saccharine group, has always led to the belief that it was not properly classed among these.

Recent investigations have given it a place by the side of glycerine, the sweet principle of fats and oils, as will be seen hereafter.

Glycyrrhizine, the sweet principle of the liquorice root, somewhat resembles mannite, but does not crystallise.

GUN-COTTON AND SUBSTANCES ALLIED TO IT.

368. Starch, the sugars, and cellulose, when acted on by the strongest nitric acid, furnish compounds which are remarkable for their explosive character, and are formed by the substitution of nitric peroxide (NO_4) for a portion of the hydrogen. By far the most important of these is *pyroxyline* (πῦρ, *fire*, ξύλον, *wood*), which is produced by the action of nitric acid upon the different forms of woody fibre, including wood, cotton, and paper.

If a piece of white unsized paper (filter-paper) be soaked for a few minutes in the strongest nitric acid (sp. gr. 1·52), then washed in a large volume of water and allowed to dry, it will be found to have suffered little alteration in appearance or texture, but to have acquired the property of burning with almost explosive violence on the application of a flame or even of a moderately heated glass rod. This is due to the presence, in the altered paper, of a quantity of oxygen in the form of NO_4 (nitric peroxide), which serves to burn up the paper very rapidly, rendering it in great measure independent of any extraneous supply of oxygen. The NO_4 has been introduced into the paper in the place of an equivalent quantity of hydrogen, which has been converted into water by the fifth equivalent of oxygen in the nitric acid ($HO.NO_5$).

The pyroxyline so obtained, however, is always associated with a quantity of unaltered paper, for the water which is formed by the oxidation of the hydrogen, dilutes the remaining nitric acid, so that unless a very large proportion of nitric acid were employed, the acid would become so far weakened towards the close of the operation as to be incapable of converting the last portions of paper into pyroxyline. Moreover, since each fibre composing the paper is a very minute tube, often folded several times, it is not possible for the nitric acid to penetrate its entire substance unless the paper be soaked in it for a long time.

In order to effect a more complete conversion of the woody fibre into pyroxyline, the nitric acid must be mixed with strong sulphuric acid, which will combine with the water produced by the action of the nitric acid upon the hydrogen of the fibre, and will thus virtually maintain the nitric acid at its greatest strength throughout the operation. Cotton wool, from the looseness of its texture, is more easily converted into pyroxyline than paper.

The following proportions may be recommended for the preparation of gun-cotton on a small scale:—Dry 1000 grains of pure nitre (p. 428) at a very moderate heat,

place it in a dry retort (fig. 274), pour upon it 10 drms. (by measure) of strong sulphuric acid, and distil until 6 drms. of nitric acid have passed over into the receiver. Dry some pure cotton wool, and weigh out 30 grains of it. Mix 2½ measured drachms of the nitric acid with an equal volume of strong sulphuric acid in a small beaker. Allow the mixture to cool, immerse the cotton wool, pressing it down with a glass rod, cover the beaker with a glass plate, and set it aside for fifteen minutes. Lift the cotton out with a glass rod, throw it into a pint of water, and wash it thoroughly in a stream of water till it no longer tastes acid or reddens blue litmus paper. Dry the cotton by exposure to air or at a very moderate heat.

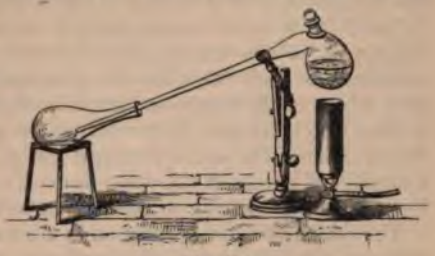


Fig. 274.

Very great attention has been paid to the manufacture of gun-cotton during the last few years, with the object of producing a perfectly uniform product which might be employed as a substitute for gunpowder.

The following is an outline of the process now generally adopted for the production of large quantities of gun-cotton :—

369. *Manufacture of gun-cotton.*—The cotton is employed in the form of loose skeins of about three ounces each, which are thoroughly cleansed by immersion for about 15 minutes in a boiling solution of carbonate of potash, containing 1 lb. of carbonate to 3 gallons of water (sp. gr. 1·02). This alkaline liquor would dissolve greasy and resinous substances, and the lignine derived from any seed entangled in the cotton, these substances imparting a brown colour to the solution. In order to avoid the necessity of wringing the skeins by hand, they are placed in a centrifugal machine (p. 498), which is a cylinder made of iron or copper gauze, through which the liquid is whirled out by the rapid rotation of the cylinder upon an axle. The skeins are then washed in running water, again whirled in the centrifugal machine, dried in a warm air chamber, and transferred to stoneware jars, with air-tight lids to prevent absorption of moisture.

The proportions in which it is found most advantageous to mix the nitric and sulphuric acids are 1 part of nitric acid (sp. gr. 1·52) and 3 parts by weight (or 2·45 by volume), of sulphuric acid (sp. gr. 1·84). These proportions of the acids are placed in separate stoneware cisterns with taps, and allowed to run simultaneously, in slow streams, into another stoneware cistern furnished with a tap and an iron lid, through a second opening in which an iron stirrer is employed to mix the acids thoroughly. The mixture is set aside for several hours to become perfectly cool.

A quantity of the mixed acids is drawn off into a deep stoneware pan standing in cold water, and provided with a perforated iron shelf, upon which the cotton may be drained. The prepared skeins are immersed, two at a time, in the acid, and stirred about in it for two or three minutes with an iron stirrer. They are then placed upon the perforated shelf, and the excess of acid squeezed out of them with the stirrer. Enough acid is drawn from the cistern to replace that which has been absorbed by the two skeins, and two more skeins are treated in the same way. Since a considerable rise of temperature is produced by the action of the nitric acid upon the cotton, it is necessary to keep the pan surrounded with cold water. A large proportion of the cotton is doubtless converted into gun-cotton in

this preliminary immersion in the mixed acids; but in order to convert the remainder, it is necessary to allow the cotton to remain in contact with the acid for a much longer period, so as to ensure its penetration into every part of the minute twisted tubes of the fibre. The preliminary immersion of each skein has the advantage of wetting every part with the acid, which could not be so certainly effected if several skeins were thrown at once into a jar, and of preventing the great accumulation of heat which would ensue if the entire chemical action were allowed to take place upon a number of skeins at the same time. The amount of heat evolved during the subsequent soaking in acid is comparatively small.

The skeins are next transferred to a jar with a well-fitting cover, in which they are pressed down and completely covered with the mixed acids, of which from 10 to 15 times the weight of the cotton will be required, according to the closeness with which the skeins are packed in the jar. The jar is placed in cold water, and the cotton allowed to remain in the acid for 48 hours.

The skeins are then removed, with the aid of an iron hook, to the centrifugal machine, in which they are whirled, at first slowly, and afterwards at 800 revolutions per minute, during ten minutes, when the bulk of the acid is separated. In order to wash away the remainder of the acid, each skein is rinsed very rapidly in a large volume of water; for if the water were allowed to come slowly into contact with the mixed acids, so much heat would be evolved as to decompose a portion of the pyroxyline; the washing by hand is continued in a stream of water until the cotton no longer tastes acid, and the skeins are then allowed to remain suspended in the stream for 48 hours.

After having been drained in the centrifugal machine, they are boiled for a few minutes in a solution of 1 lb. of carbonate of potash in 3 gallons of water, to neutralise any remaining trace of acid,* again drained in the centrifugal machine, and left in the stream for about a fortnight. The gun-cotton is then dried by exposure to air.

Divested of merely mechanical details, the manufacture of gun-cotton seen to consist of the following essential operations:—

(1.) Cleansing the cotton by boiling with carbonate of potash, and subsequent washing with water.

(2.) Immersion for two or three minutes in a mixture of strongest nitric acid with three times its weight of strongest sulphuric acid.

(3.) Soaking for 48 hours in a fresh portion of the mixed acids.

(4.) Thorough washing with water.

(5.) Boiling with carbonate of potash.

(6.) Thorough washing and drying.

In the opinion of some manufacturers, it is advantageous to impregnate the finished gun-cotton with a solution of silicate of soda, to dry it, and then wash it with water. It was supposed that the silicate of soda was decomposed, partly by lingering traces of acid in the cotton, partly by the action of atmospheric carbonic acid, a minute quantity of silica being thus deposited in the fibre, which had the effect of retarding the combustion to a desirable extent, and of diminishing the tendency of the cotton to absorb moisture from the air. Experiments instituted by Abel appear to prove that the advantages of this silicating process are altogether imaginary.

* The alkaline bath would also remove any resinous substances produced by the action of the nitric acid upon the seed, &c., accidentally left in the original cotton.

0. *Chemical composition of gun-cotton.*—Perfectly pure gun-cotton ains carbon, hydrogen, nitrogen, and oxygen, in proportions which spond to the empirical formula $C_{12}H_7N_3O_{22}$. The determination of ational formula is attended with difficulty, because, being an indiffe- substance, it does not form definite combinations with other bodies own equivalent weight, and it is of course impossible to arrive at its ne in the state of vapour, which so frequently affords valuable assist- n fixing a rational formula. Having regard to the mode of its for- n from cellulose (cotton), $C_{12}H_{10}O_{10}$, by the action of nitric acid, ut evolution of gas, the most probable rational formula appears to be $(NO_4)_3O_{10}$, which represents it as *trinitrocellulose*, or cellulose in a three equivalents of nitric peroxide have been substituted for three drogen. The action of nitric acid upon the cotton would then be sented by the equation—

$$\underset{\text{Cellulose.}}{C_{12}H_{10}O_{10}} + 3(HO.NO_5) = \underset{\text{Trinitrocellulose.}}{C_{12}H_7(NO_4)_3O_{10}} + 6HO.*$$

cording to this equation, 100 lbs. of cotton should furnish 183 lbs. n-cotton; but in practice only about 177 lbs. are obtained, a part of eficiency being accounted for by unavoidable mechanical loss, and by quantities of foreign matters dissolved out by the acids.

at the nitrogen is really present in the gun-cotton in the form of peroxide (NO_4), as implied in the above formula, is indicated by ction of potash, which dissolves the gun-cotton, and yields a solution ining nitrate and nitrite of potash, exactly the products which are d by the action of potash upon nitric peroxide (p. 135).

nother reaction of gun-cotton which supports the above view of its itution, is that with hydrosulphate of potassium. If some hydrate of h be dissolved in alcohol, and the solution saturated with gaseous osulphuric acid, an alcoholic solution of hydrosulphate of potassium HS) is obtained; and if the gun-cotton be immersed in this solution, ently heated, it will be rapidly reconverted into ordinary cotton, and e of potash will be found in the solution—

$$\underset{\text{Trinitrocellulose.}}{C_{12}H_7(NO_4)_3O_{10}} + 3(KS.HS) = \underset{\text{Cellulose.}}{C_{12}H_{10}O_{10}} + 3(KO.NO_5) + S_6.$$

is is the so-called synthetical method of determining the composition n-cotton, for of course 183 parts of the latter should furnish 100 parts ton.

1. *Products of the explosion of gun-cotton.*—From what has been l with respect to the products of explosion of gunpowder (p. 423), ght be expected that those furnished by gun-cotton would vary ding to the conditions under which the explosion takes place. n a mass of the cotton is exploded in an unconfined state, the sion is comparatively slow (though appearing to the eye almost in- aneous), since each particle is fired by the flame of that immediately ning it, the heated gas (or flame) escaping outwards, so that some elapses before the interior of the mass is ignited. But when the otton is enclosed in a strong case, so that the flame from the portion gnited is unable to escape outwards and must spread into the interior s mass, this is ignited simultaneously at a great number of points, he decomposition takes place far more rapidly; a given weight of

* atomic symbols and the unitary formula for nitric acid be employed, the equation become $\Theta_6H_{10}\Theta_5 + 3HN\Theta_3 = \Theta_6H_7(N\Theta_2)_3\Theta_5 + 3H_2\Theta$.

cotton being thus consumed in a much shorter time, a far higher tem
ture is produced, and the ultimate results of the explosion are much
complex, as would be expected from the well-known simplifying effe
high temperatures upon chemical compounds.

Some of the earliest experiments upon gun-cotton showed that wh
was fired in a loose state, nitric oxide, nitrous acid, hydrocyanic acid,
were discoverable among the gaseous products, and gave rise to melanc
forebodings of injury to miners and gunners from the inhalation of
poisonous vapours. Further experience has proved that no objection
be made to the use of gun-cotton on this ground, for when it is emplo
either in fire-arms or in blasting, it is of necessity fired in a confi
state, and the products are simply aqueous vapour, carbonic acid, carb
oxide, and nitrogen, with a little marsh-gas and hydrogen.

The determination of the products of explosion of confined gun-co
has been effected by Karolyi in the same manner as in the case of
powder (*see* p. 424), by enclosing the cotton in a cast-iron cylinder, s
enough to resist bursting until the combustion of the last portio
the charge, which was suspended in an iron globe exhausted o
and exploded by the galvanic battery; the total volume of the
collected in the globe was then determined and subjected to an
The amount of gun-cotton fired was about 150 grains. Unfortu
the formula given for the sample of gun-cotton experimented on do
represent the trinitrocellulose which constitutes pure gun-cotton,
$C_{24}H_{17}N_3O_{35}$, instead of $C_{24}H_{14}N_6O_{44}$ (representing 2 eqs. of trinitrocell
but the difficulty attending the exact ultimate analysis of gun-cotto
great, that there is greater probability of the analysis being incorre
of the composition of the cotton having really differed material
that of trinitrocellulose. 100 grains of gun-cotton gave a quan
aqueous vapour and gaseous products, calculated to occupy, at
and 29·06 in. Bar., 325·5 cubic inches, supposing the aqueous va
remain uncondensed at that temperature. The analysis of the ga
that 100 volumes of the products of explosion contain—

Aqueous vapour,	25·34 vols.
Carbonic oxide (CO),	28·95 ,,
Carbonic acid (CO_2),	20·82 ,,
Nitrogen,	12·67 ,,
Hydrogen,	3·16 ,,
Marsh-gas (C_2H_4),	7·24 ,,
	98·18 ,,

The amount of aqueous vapour was inferred from that of the
contained in the gun-cotton.

If the marsh-gas and hydrogen be left out of consideration, th
ing equation will account for the other products of the explo
posing the gun-cotton to be pure trinitrocellulose—

$$C_{12}H_7(NO_4)_3O_{10} = 9CO + 3CO_2 + 7HO + N_3.$$

According to this equation, 100 grains of gun-cotton should fu
cubic inches of gas and vapour, instead of 325·5 as determined b
ment, and the volumes of the products should be—

Aqueous vapour,	28 vols.
Carbonic oxide,	36 ,,
Carbonic acid,	12 ,,
Nitrogen,	12 ,,

do not agree with the experimental results. It is not to be ex-
, however, that one simple equation should correctly represent all
›ducts of such a decomposition (*see* p. 425).

ıas been stated* that, practically, gun-cotton is most effective in
when of such density that 11 lbs. occupy a cubic foot. One cubic
ould then weigh 44·5 grains, and would evolve (calculating from
sult of Karolyi's experiment) a quantity of steam and gas which
occupy 140·5 cubic inches at 60° F. and 30 in. Bar., supposing the
to be capable of remaining uncondensed.

ras calculated at p. 426, that one cubic inch of gunpowder, or 235
(58 lbs. to the cubic foot), would evolve 207 cubic inches of gas
red at 60° F. and 30 in. Bar.

s much to be regretted that, up to the present time, no one has
ded in determining the heat evolved in the explosion of a given
t of gun-cotton, so that it is impossible to calculate the volume which
oducts would occupy at the instant of the explosion, and therefore
echanical effect which the expanded gases are capable of producing.
›posing the products of explosion to be equally expanded by heat
moment of explosion, it would appear at first sight that gunpowder
l produce a greater mechanical effect than an equal weight of gun-
—

grs. of gun-cotton occupying 1·0 cub. in. evolve 140·5 cub. in. of gas (cooled)
„ gunpowder „ 0·2 „ „ 207 „ „ „

h charges were confined in spaces which they exactly filled, the
ires exerted would be 1035 atmospheres for gunpowder, and 140·5
pheres for gun-cotton.

›erience, however, has shown that a given weight of gun-cotton pro-
three times the effect, in artillery, of an equal weight of gunpowder.
count for this, it might be supposed that the heat evolved in the
ıstion of the cotton exceeds that produced by gunpowder, so that
ıgh the gas from the latter is calculated to exert a higher pressure at
dinary temperature, it is less heated and expanded at the moment
›losion, and therefore exerts less pressure than the gas from gun-
. Without any such assumption, however, the superior power of
›tton in artillery may be explained by the more complete explosion
entire charge, and by the greater rapidity of its combustion.

s well known that a very large proportion of the charge of gun-
r is blown out of the gun unburnt, whereas, by proper management,
particle of the gun-cotton may be consumed.

the greater rapidity of the combustion of gun-cotton is probably
ost important reason for its greater mechanical effect, since the entire
ıe of the gas would be evolved before the confining space was ma-
y enlarged by the movement of the projectile, which would thus be
ed to the maximum pressure. Indeed, this rapidity of combustion
to the nature of gun-cotton as a chemical compound, and not a
ınical mixture like gunpowder) was the chief obstacle to its use in
ry, since it frequently burst the gun in the earlier trials, until it
liscovered that, by spinning and weaving the yarn into webs of
ıs degrees of closeness, the rate of combustion could be modified as
f gunpowder is by granulation; so that whilst the loose yarn burns
open air at the rate of 1 foot per second; when twisted into thread

* *Report of the Gun-cotton Committee to the British Association*, 1863.

and woven into a web for cartridges, it burns in the open air at the rate of 10 feet per second, and this rate may be varied by varying the tightness with which the thread is twisted. When the charge is confined in a gun, however, the results are not so satisfactory, since the great pressure of the gas first generated drives the flame through the mass of cotton, and produces almost instantaneous ignition throughout, resulting in serious damage to the bore of the gun. It has been found preferable, in making cartridges for fowling-pieces, to dilute the gun-cotton by mixing it with some unconverted cotton. Abel reduces the gun-cotton to a pulp similar to that used by paper-makers, in which state, it may, if necessary, be diluted with ordinary cotton in pulp, and may be compressed into very compact, slowly burning cakes, in which it offers great advantages for making up a charge.

In mining operations, such as blasting rocks, it is said that gun-cotton produces the same effect as six times its weight of gunpowder; and since, in such cases, the space confining the charge is incapable of gradual enlargement, the rate of combustion is not of so much importance as the maximum pressure to which the gas is capable of attaining, so that this result can hardly be explained unless it be supposed that the heat evolved in the combustion of the cotton is really greater than that furnished by gunpowder—an assumption which is scarcely consistent with the fact that guns are much less heated by firing a certain number of rounds with gun-cotton than they would be with gunpowder. It must not be forgotten, however, that since gun-cotton leaves no solid products of explosion, the entire amount of heat, whatever that may be, is available for the expansion of the gaseous products, giving it a great advantage over powder, of which the solid products have, of course, to be raised to the same temperature as the gases, without contributing to increase the mechanical effect by their expansion.

If the end of a strand of gun-cotton yarn be kindled at a very few points of the filaments, by a spark on touch-paper, or at the end of a piece of string, it will undergo a very slow smouldering combustion, as first observed by Abel; and if the experiment be made in a narrow glass tube closed at one end, the carbonic oxide may be kindled at the mouth of the tube, whilst the cotton is smouldering inside.

372. *Properties of gun-cotton compared with those of gunpowder.*—Gun-cotton is more easily exploded than gunpowder; the latter requires a temperature of at least 600° F., whilst gun-cotton may explode at 277° F., and must explode at 400° F. It is very difficult to explode gunpowder by percussion, even between a steel hammer and anvil; but gun-cotton invariably detonates in this way, though the explosion is confined to the part under the hammer. The explosion of gun-cotton is, of course, unattended by any smoke, a most important advantage in mines, the atmosphere of which is sometimes rendered almost intolerable by the smoke of gunpowder used in blasting. The absence of residue from the gun-cotton prevents the fouling of guns, and renders it unnecessary to sponge them after each discharge, for the amount of incombustible mineral matter present in the cotton is very small (from 1 to 2 per cent.), and is entirely scattered by the explosion.

It has already been mentioned that the explosion of gun-cotton does not impart so much heat to the metal of the gun as that of powder, the difference being so great that, after firing 100 rounds with gun-cotton, the gun

was not so much heated as after 30 rounds with gunpowder. This important advantage of gun-cotton has been explained by some to depend upon the very high specific heat of the aqueous vapour, which forms so large a portion of the products of explosion. For since the specific heat of steam is 0·48, and that of carbonic oxide (which, among the products from gunpowder, has the highest specific heat) is 0·25, nearly twice as much heat would be consumed in raising the former to a given temperature as in raising the latter; but it is hardly necessary to account for the result in this manner, when it is remembered that the charge of gun-cotton is only one-third of the charge of powder, that the explosion of the former is so much more rapid, leaving less time for the communication of heat to the metal, and that there are no highly-heated solid products left in contact with the gun. Gun-cotton may be fired upon the palm of the hand with impunity, or upon a heap of gunpowder without kindling it; although it cannot be doubted that the temperature of the flame is really much higher than the inflaming point of powder. That the recoil of a gun charged with gun-cotton is only two-thirds of that experienced with gunpowder, is a matter for the consideration of the artillerist rather than the chemist. The fact that if gun-cotton be used to effect a breach in palisades, &c., it must be confined in a strong case, whereas gunpowder in a bag would suffice for the work of demolition, is explained by what has been stated at p. 503, viz., that the flame tends outwards so rapidly from loosely-confined gun-cotton, that its explosion is too gradual, and it then produces less effect than powder; but when tightly confined, the flame, unable to escape, pervades the whole mass, and a nearly instantaneous explosion is the result.

It is evident, from the consideration of its manufacture, that gun-cotton is entirely uninjured by water, so that a store of this explosive might be immersed in water in case of need, and would be still serviceable after drying, whereas gunpowder is, of course, rendered useless by contact with water, which dissolves out the nitre. Even when exposed to very damp air, gunpowder is liable to injury from the effect of moisture in partially separating the nitre from the other ingredients, whilst gun-cotton only requires exposure to a dryer atmosphere for a short time to render it fit for use. The proportion of moisture retained by gun-cotton, in the ordinary state of the atmosphere, is 2 per cent.

As an objection to the employment of gun-cotton as a substitute for gunpowder, it has been asserted that the trinitrocellulose is liable to undergo spontaneous decomposition, which might at any time render the contents of a magazine unserviceable, or might even give rise to the evolution of a sufficient amount of heat to cause an explosion. The origin of this objection is to be traced to the old process for preparing gun-cotton, in which the acids were not allowed to act upon the cotton for a sufficient length of time, so that the whole of the cotton was not converted into true gun-cotton, but some less stable substitution products were formed at the same time. Another cause of spontaneous alteration is the imperfect washing of the gun-cotton, whereby minute traces of acid are left in the fibre. All recent experiments, by Abel and others, appear to have proved that, considering its highly complex character, gun-cotton is a very stable compound under ordinary conditions; although, when kept in a moist state, it developes traces of acid products, the temperature does not rise to any important extent, nor is the explosive quality of the material at all *injured*.

373. Gun-cotton is somewhat harsher to the touch than ordinary cotton, and becomes remarkably electrical when rubbed between the dry fingers. It is insoluble in alcohol and ether, as well as in a mixture of these solvents, though ordinary specimens generally yield a small percentage of soluble matter when treated with a mixture of alcohol and ether, because they contain extraneous matters, such as the other substitution products to be mentioned presently. Acetic ether dissolves it, and so does a mixture of ordinary ether with ammonia. Strong sulphuric acid dissolves it without carbonisation, unless any unconverted cotton should happen to be present.

374. *Collodion-cotton.*—When cotton or paper is acted upon by a mixture of nitric and sulphuric acids containing more water than is present in that employed for the preparation of gun-cotton (p. 501), compounds are formed which contain less nitric peroxide, and are much less combustible than the trinitrocellulose, from which they are also distinguished by their solubility in mixtures of alcohol and ether.

In order to render evident the relations between these compounds and gun-cotton, the formula of the latter must be trebled, when we have the following series of nitro-compounds produced by the mixtures of nitric acid, sulphuric acid and water, to which they stand opposite—

Composition of the mixed acids.	Products of their action on cellulose.
(1.) $HO.NO_5 + 2(HO.SO_3)$	$C_{36}H_{21}(NO_4)_9O_{30}$
(2.) $HO.NO_5 + 2(HO.SO_3) + 3\frac{1}{2}HO$	$C_{36}H_{22}(NO_4)_8O_{30}$
(3.) $HO.NO_5 + 2(HO.SO_3) + 4HO$	$C_{36}H_{23}(NO_4)_7O_{30}$
(4.) $HO.NO_5 + 2(HO.SO_3) + 5HO$	$C_{36}H_{24}(NO_4)_6O_{30}$

As might be expected, these compounds diminish in combustibility in proportion as the NO_4 contained in them diminishes. The second is that employed for the preparation of photographic collodion, being dissolved for that purpose in a mixture of ether and alcohol.

In order to prepare the soluble cotton for collodion, three measured ounces of ordinary nitric acid (sp. gr. 1·429) are mixed with two ounces of water in a pint beaker. Nine measured ounces of strong sulphuric acid (sp. gr. 1·839) are added to this mixture, which is continually stirred whilst the acid is being added. A thermometer is placed in the mixture, which is allowed to cool to 140° F.; 100 grains of dry cotton wool, in ten separate tufts, are immersed in the mixture for five minutes, the beaker being covered with a glass plate. The acid is then poured into another beaker, the cotton squeezed with a glass rod, and thrown into a large volume of water; it is finally washed in a stream of water till it is no longer acid, and dried by exposure to air. (By adding to the acid which was drained out of the cotton, three drachms more sulphuric acid, and immersing another 100 grains of cotton for *ten* minutes, a second portion of soluble cotton may be obtained.)

Collodion balloons.—These balloons may be made in the following manner:—6 grains of the collodion cotton, prepared according to the above directions, are dissolved in a mixture of 1 drachm of alcohol (sp. gr. ·835) and 2 drachms of ether (sp. gr. ·725), in a corked test-tube. The solution is poured into a dry Florence flask, which is then turned about slowly so that every part of its surface may be covered with the collodion, the excess of which is then allowed to drain back into the tube. Air is then blown into the flask through a long glass tube attached to the bellows (or to the blowpipe-table, fig. 116) as long as any smell of ether is perceptible. A pen-knife blade is carefully inserted between the flask and the neck of the balloon, which is thus detached from the glass all round; a small piece of glass tubing is introduced for an inch or two into the neck of the balloon, so that the latter may cling round it. Through this tube air is drawn out by the mouth until one-half of the balloon has left the side of the flask and collapsed upon the other half; by carefully twisting the tube, the whole of the balloon may be detached and drawn out through the neck

flask, when it must be quickly untwisted, distended by blowing through the tied with a piece of silk, and suspended in the air to dry. The average weight balloons is two grains.

When collodion-cotton is kept for some time, especially if at all damp, undergoes decomposition, filling the bottle with red fumes, and becoming verted into a gummy mass, which contains oxalic acid.

375. *Xyloidine* is the name given to a highly combustible substance alogous to pyroxyline, which is obtained by dissolving starch in the ongest nitric acid, and diluting the solution with water, when the loidine falls as a white precipitate, which may be collected upon a er, and washed till free from acid. The composition of xyloidine is $H_5(NO_4)_5O_{10}$, representing starch ($C_{12}H_{10}O_{10}$), in which 2 equivalents of tric peroxide have been substituted for 2 equivalents of hydrogen.

Nitromannite ($C_{12}H_8(NO_4)_6O_{12}$) is another explosive body of the same der, obtained by adding powdered mannite ($C_{12}H_{14}O_{12}$), in small portions, a mixture of equal measures of the strongest nitric and sulphuric acids, hich immediately dissolve it, and presently solidify to a mass of minute edles of nitromannite, which may be washed with a large volume of ater, and crystallised from boiling alcohol. Under the hammer, nitro- annite explodes with a very loud report. When heated, it fuses before ploding.

WINE AND SPIRITS.

376. Wine is essentially composed of 8 or 10 parts of alcohol, with 5 or 90 of water, together with minute quantities of certain fragrant thers, of colouring matter, of bitartrate of potash, and of the mineral ubstances derived from the grape-juice. Glycerine and succinic acid ave also been found in wines, and appear to be constant secondary pro- ucts of the alcoholic fermentation.

Those wines in which the whole of the sugar has been fermented are known as *dry* wines; whilst *fruity* wines still retain a considerable quantity of sugar.

The preparation of wine differs from that of beer in the circumstance that no addition of ferment is necessary, the fermentation being excited by a substance present in the grape-juice. This juice contains, in addition to grape-sugar, vegetable albumen, tartrate of potash, and the usual mineral salts found in vegetable juices. The husks, seeds, and stalks of the grape contain a considerable quantity of tannin, together with certain blue, red, and yellow colouring matters.

When the expressed juice remains for a short time in contact with the air, the albuminous substances contained in it enter upon a state of change, exciting the vinous fermentation in the sugar, and a scum of yeast is formed upon the surface. If this fermentation takes place in contact with the husks of the dark grapes, the alcohol dissolves the colouring matter, and a red wine results; whilst for the production of white wines, the husks, &c., are separated previously to the fermentation, and the juice is exposed as little as possible to the air.

White wines are rather liable to become *ropy* from viscous fermentation, but this is prevented by the addition of a small quantity of tannin, which precipitates the peculiar ferment. The tannin for this purpose is extracted from the husks and stalks of the grapes themselves.

Red wines, such as port and claret, are often very astringent from the tannin dissolved out of the husks, &c., during the fermentation. Port wine, when freshly bottled, still retains in solution a considerable quantity of bitartrate of potash ($KO.HO.C_8H_4O_{10}$), but after it has been kept some time, and become more strongly alcoholic, this salt is deposited together with a quantity of the colouring matter, in the form of a crust upon the side of the bottle. Thus a dark *fruity* port becomes *tawny* and *dry* when kept for a sufficient length of time, the sugar having been converted into alcohol.

When the wine contains an excess of tartaric acid, it is customary to add to it some neutral tartrate of potash ($2KO.C_8H_4O_{10}$), which precipitates the acid in the form of bitartrate.

The preparation of champagne is conducted with the greatest care. The juice or *must* is carefully separated from the *marc* or husk, and is often mixed with one per cent. of brandy before fermentation. After about two months the wine is drawn off into another cask, and clarified with isinglass dissolved in white wine, and added in the proportion of about half-an-ounce to 40 gallons. This combines with the tannin to form an insoluble precipitate, which carries with it any impurities floating in the wine. After another interval of two months, the wine is again drawn off, and a second clarification takes place, and in two months more the wine is drawn off into bottles containing a small quantity of pure sugar-candy dissolved in white wine. The bottles, having been securely corked and wired, are laid down upon their sides for eight or ten months, during which time the fermentation of the newly added sugar takes place, and the carbonic acid produced dissolves in the wine, whilst a quantity of yeast is separated. In order to render the wine perfectly clear, the bottle is left for about three weeks in such a position that the deposit may subside into the neck, against the cork, which is then unwired so that the pressure of the accumulated carbonic acid may force it out together with the deposit; the bottle having been rapidly filled up with white wine, is again corked, wired, covered with tin foil, and sent into the market. Pink champagne is prepared from the must which is squeezed out of the marc after it has ceased to run freely, and contains a little of the colouring matter of the husk. The colour is also sometimes imparted by adding a little tincture of litmus.

The proportion of alcohol in wines varies greatly, as will be seen from the following statement of the weight of alcohol in 100 parts of the wine:

Port,	. .	from 15 to 17.
Sherry,	.	„ 14 to 16.
Champagne,		11·5.
Claret,	. .	„ 8 to 9.
Rudesheimer,		„ 7 to 8·5.

Sherry contains from 1 to 5 per cent. of sugar, port from 3 to 7 per cent., and Tokay 17 per cent.; in the last case, the sugar is increased by adding some of the must concentrated by evaporation to the wine previously to bottling.

The *bouquet* or fragrance of wine is due to the presence of certain fragrant ethers, especially of œnanthic, pelargonic, and acetic ether, formed during the fermentation or during the subsequent storing of the wine.

to the increased quantity of such fragrant ether that the superior quet of many old wines is due.

77. *Distilled spirits.*—The varieties of ardent spirits are obtained from mented liquids by distillation, so that they consist essentially of alcohol e or less diluted with water, and flavoured either with some of the atile products of the fermentation, or with some essential oil added the purpose.

Brandy is distilled from wine, and coloured to the required extent with nt sugar (caramel). Its flavour is due chiefly to the presence of nthic ether derived from the wine. The colour of genuine pale ndy is due to its having remained so long in the cask as to have dis-ed a portion of brown colouring matter from the wood, and is there-an indication of its age. Hence arose the custom of adding caramel, sometimes infusion of tea, to impart the astringency due to the tannin lved from the wood by old brandy.

Whisky is distilled from fermented malt, which has been dried over a fire, to which the characteristic smoky flavour is due.

Gin is also prepared from fermented malt or other grain, and is flavoured the essential oil of juniper, derived from juniper berries, added during distillation.

Rum is distilled from fermented molasses, and appears to owe its our to the presence of butyric ether, or of some similar compound.

Arrack is the spirit obtained from fermented rice.

Kirschwasser and *maraschino* are distilled from cherries and their es, which have been crushed and fermented.

ome varieties of British brandy and whisky are distilled from fer-ted potatoes, or from a mixture of potatoes and grain, when there ls over, together with ordinary alcohol, another spirit belonging to same class, but distinguished from alcohol by its nauseous and irritat-odour. This substance, which is known as *potato-spirit, amylic hol*, or *fousel oil* ($C_{10}H_{12}O_2$) also occurs, though in very minute ntity, in genuine wine-brandy. The manufacturers of spirit from grain potatoes remove a considerable part of this disagreeable and unwhole-substance by leaving the spirit for some time in contact with wood-coal.

THE ALCOHOLS AND THEIR DERIVATIVES.

78. It has already been stated that alcohol is the type of a very im-ant class of compounds closely related to each other in composition properties.

he alcohols are all composed of carbon, hydrogen, and oxygen; the bers of the series represented by common alcohol always contain two valents of oxygen, and two more equivalents of hydrogen than of on. The number of equivalents of carbon and hydrogen is always an number, so that the *general formula of an alcohol of this series* may written thus, $C_{2n}H_{2n+2}O_2$. Thus, in ordinary or *vinic* alcohol, $_2O_2$, $n = 2$, in wood-spirit or *methylic* alcohol, $C_2H_4O_2$, $n = 1$, in to-spirit or *amylic* alcohol, $C_{10}H_{12}O_2$, $n = 5$.

hese alcohols constitute, therefore, a truly homologous series (p. 459) hich many members, however, remain to be discovered.

he following table includes the alcohols of this series which are at ent known :—

Chemical Name.	Source.	Equivalent Formula.	Common Name
1. Methylic alcohol	Destructive distillation of wood	$C_2H_4O_2$	Wood naphtha
2. Ethylic ,,	Vinous fermentation of sugar	$C_4H_6O_2$	Spirit of wine
3. Propylic ,,	Fermentation of grape-husks	$C_6H_8O_2$	
4. Butylic ,,	Fermentation of beet-root .	$C_8H_{10}O_2$	
5. Amylic ,,	Fermentation of potatoes . .	$C_{10}H_{12}O_2$	Fousel oil
6. Caproic ,,	Fermentation of grape-husks	$C_{12}H_{14}O_2$	
7. Œnanthic ,,	Distillation of castor-oil with potash	$C_{14}H_{16}O_2$	
8. Caprylic ,,	Fermentation of grape-husks	$C_{16}H_{18}O_2$	
10. Rutic ,,	Oil of rue	$C_{20}H_{22}O_2$	
12. Lauric ,,	Whale oil	$C_{24}H_{26}O_2$	
16. Cetylic ,,	Spermaceti	$C_{32}H_{34}O_2$	Ethal
27. Cerylic ,,	Chinese wax	$C_{54}H_{56}O_2$	Cerotene
30. Melissic ,,	Bees' wax	$C_{60}H_{62}O_2$	Melissine

The usual gradation in properties attending the gradation in composi among the members of a homologous series, is strikingly exemplified i class of alcohols. The first eight members of the group, linked tog as they are by an almost common origin (being derived, with one excep from the fermentation of substances nearly allied, and that exception a product of destructive distillation which may be regarded as an ac ated fermentation), and by a regularly ascending composition, wou expected to resemble each other in their properties far more closely the other members of the class. Accordingly, we find that met ethylic, propylic, butylic, amylic, caproic, œnanthic,* and caprylic alc are all liquid at the ordinary temperature, that they all possess pe and powerful odours, and may be readily distilled unchanged. A these, however, the gradation is not to be overlooked. The two methylic and ethylic alcohols, may be mixed with water in all propor but the third, propylic alcohol, though freely soluble in water, is to an unlimited extent; whilst butylic alcohol is less soluble, and alcohol may be said to be sparingly soluble in water. Caproic al the next member, is insoluble in water; whilst caprylic is not only inso but possseses an oily character, leaving a greasy stain upon paper.

In their boiling points, and the specific gravities of their vap similar gradation is observed.

Alcohol.	Boiling Point.	Vapour Density.
Methylic, ...	149°·9 F.	1.12
Ethylic, ...	178°	1·61
Propylic, ...	205°	2·02
Butylic, ...	238°	2·59
Amylic, ...	269°·8	3·15
Caproic, ...	299°–309°	3·53
Œnanthic, ...	327°–348°	—
Caprylic, ...	356°	4·50

* This alcohol is of recent discovery, and has been little examined.

equivalent of each of these alcohols yields *four volumes** of vapour; other words, if a given weight of the alcohol corresponding to its lent number be converted into vapour, that vapour will occupy four as much space as would be occupied by an equivalent of oxygen at ne temperature and pressure, or twice the space occupied by an lent of hydrogen, or of water converted into vapour under the onditions.

higher members of the group of alcohols are solid fusible bodies early approaching to waxy or fatty matters in their nature, and not tible of distillation without decomposition. Far less is known of han of the alcohols containing less carbon.

true chemical definition of an alcohol of this series rests upon the stance, that under the influence of oxidising agents, it first parts wo equivalents of hydrogen, and is converted into an *aldehyde* ol dehydrogenated), and afterwards absorbs two equivalents of n, yielding an acid. Thus, it has been already shown (p. 492), that lcohol ($C_4H_6O_2$), when exposed to air under favourable conditions, aldehyde, $C_4H_4O_2$, which, by absorbing oxygen, is converted into acid, $C_4H_4O_4$.

formation of an aldehyde would, therefore, be represented by the l formula—

$$\underset{\text{Alcohol.}}{C_{2n}H_{2n+2}O_2} + O_2 = \underset{\text{Aldehyde.}}{C_{2n}H_{2n}O_2} + 2HO,$$

at of the corresponding acid by

$$\underset{\text{Alcohol.}}{C_{2n}H_{2n+2}O_2} + O_4 = \underset{\text{Acid.}}{C_{2n}H_{2n}O_4} + 2HO.$$

ddition to this, each of these alcohols, by the loss of the elements of quivalent of water, yields an *ether*, corresponding to ordinary ether), which differs from vinic alcohol, $C_4H_6O_2$, by the elements of an lent of water.

general formula representing the derivation of an ether from an l of the above series is—

$$\underset{\text{Alcohol.}}{C_{2n}H_{2n+2}O_2} - HO = \underset{\text{Ether.}}{C_{2n}H_{2n+1}O}.$$

ce every alcohol has its corresponding aldehyde, acid, and ether, so here are homologous series of aldehydes, acids, and ethers, just as alcohols from which they are derived.

only members of the aldehyde and ether series which have received e share of attention on account of their practical importance, are derived from ordinary alcohol; but the series of acids contains many ers of importance, to some of which no corresponding alcohols t known.

very important homologous series of acids† composed after the l formula $C_{2n}H_{2n}O_4$, includes—

* Or one molecule of each alcohol yields two volumes (H = 1 vol.).

† *Often spoken of as the acetic series of acids*, or the *fatty acid series*.

Acid.	Source.	Equivalent Formula.
1. Formic acid,	Red ants, nettles . . .	$C_2H_2O_4$
2. Acetic „	Vinegar	$C_4H_4O_4$
3. Propylic „	Oxidation of oils	$C_6H_6O_4$
4. Butyric „	Rancid butter	$C_8H_8O_4$
5. Valerianic acid	Valerian root	$C_{10}H_{10}O_4$
6. Caproic „	Rancid butter	$C_{12}H_{12}O_4$
7. Œnanthic „	Oxidation of castor oil . .	$C_{14}H_{14}O_4$
8. Caprylic „	Rancid butter	$C_{16}H_{16}O_4$
9. Pelargonic acid	Geranium leaves	$C_{18}H_{18}O_4$
10. Rutic or capric acid	Rancid butter	$C_{20}H_{20}O_4$
11. Euodic* „	Oil of rue	$C_{22}H_{22}O_4$
12. Lauric „	Bay berries	$C_{24}H_{24}O_4$
13. Cocinic „	Cocoa nut oil	$C_{26}H_{26}O_4$
14. Myristic „	Nutmeg butter	$C_{28}H_{28}O_4$
15. Benic „	Oil of ben	$C_{30}H_{30}O_4$
16. Palmitic „	Palm oil	$C_{32}H_{32}O_4$
17. Margaric „	Olive oil?	$C_{34}H_{34}O_4$
18. Stearic „	Tallow	$C_{36}H_{36}O_4$
19. Balenic „		$C_{38}H_{38}O_4$
20. Butic „	Butter	$C_{40}H_{40}O_4$
21. Nardic „		$C_{42}H_{42}O_4$
27. Cerotic „	Bees' wax	$C_{54}H_{54}O_4$
30. Melissic „	Bees' wax	$C_{60}H_{60}O_4$

A very gradual transition of properties is observable in the membe this extended series of acids.

The first nine members of the series are liquid, the remainder solid at mon temperatures. Of the liquids, formic acid boils at 221° F., and the ing points of the other members exhibit a gradual rise up to pelargonic which boils at 500° F. The melting-points of the solid acids also a from 86° F. for rutic acid ($C_{20}H_{20}O_4$) to 192° F. for melissic ($C_{60}H_{60}$

Formic and acetic acids may be mixed with water in all propor like their corresponding alcohols, the methylic and ethylic; pr acid, though soluble to a great extent in water, resembles the corre ing alcohol in not mixing indefinitely with water. Butyric acid b in a similar manner. Valerianic, caproic, œnanthic, and caprylic ac sparingly soluble in water. Pelargonic and capric acids are very spa soluble, and the remaining members of the series are very decidedl *acids*, insoluble in water, and forming *soaps* with the alkalies.

The members of the series of alcohols, under the action of po dehydrating agents, are capable of parting with the elements equivalents of water, furnishing the members of a homologous se hydrocarbons related to their corresponding alcohols, as olefiant ethylene (C_4H_4) is related to ethylic alcohol.

The general formula for the production of the homologues of e (or *olefines*) from the alcohols may be thus expressed—

$$C_{2n}H_{2n+2}O_2 - 2HO = C_{2n}H_{2n}.$$

* Εὐώδης, fragrant.

e known members of this series of hydrocarbons are—

Name.	Equivalent Formula.	Corresponding Acid.	Corresponding Alcohol.
1. Methylene .	C_2H_2	Formic	Wood-naphtha
2. Ethylene .	C_4H_4	Acetic	Alcohol
3. Propylene .	C_6H_6	Propylic	Propylic
4. Butylene . .	C_8H_8	Butyric	Butylic
5. Amylene . .	$C_{10}H_{10}$	Valerianic	Fousel oil
6. Caproylene .	$C_{12}H_{12}$	Caproic	Caproic
7. Œnanthene .	$C_{14}H_{14}$	Œnanthic	Œnanthic
8. Caprylene .	$C_{16}H_{16}$	Caprylic	Caprylic
9. Elaene . .	$C_{18}H_{18}$	Pelargonic	
10. Paramylene .	$C_{20}H_{20}$	Rutic	Rutic
16. Cetylene .	$C_{32}H_{32}$	Palmitic	Ethal
27. Cerotene .	$C_{54}H_{54}$	Cerotic	Cerotene
30. Melissene .	$C_{60}H_{60}$	Melissic	Melissine

f these hydrocarbons, methylene, ethylene, and propylene are gaseous ; lene is also a gas, but easily condensed to the liquid state ; the re- der are liquid at the ordinary temperature.

is series exhibits one of the best examples of *polymerism* or multiple ion of composition, each member of the series being represented by a ula which is a multiple by some whole number of that of the first ber of the series.

nce one equivalent of each of these hydrocarbons in the state of ur occupies *four volumes*,* it must follow, if their composition be cor- y stated, that their vapour densities exhibit a multiple relation similar at which exists between their formulæ.

hat this is the case will be seen by the subjoined table, which illus- s very clearly the importance of determining the specific gravity of vapour of a volatile substance as a confirmation of the results of ysis :—

Hydrocarbon.		Specific gravity of vapour.
Methylene,	C_2H_2	0·490
Ethylene,	C_4H_4	0·978
Propylene,†	C_6H_6	1·498
Butylene,	C_8H_8	1·852
Amylene,	$C_{10}H_{10}$	2·386
Caproylene,	$C_{12}H_{12}$	2·875
Caprylene,	$C_{16}H_{16}$	3·90
Elaene,	$C_{18}H_{18}$	4·48
Paramylene,	$C_{20}H_{20}$	5·061
Cetylene,	$C_{32}H_{32}$	8·007

will be observed that just as the formula of cetylene ($C_{32}H_{32}$) is a

r one molecule occupies two volumes (H = 1 vol.).

These hydrocarbons are sometimes designated by names which refer to the multiple of which they contain. Thus propylene, $3(C_2H_2)$, is sometimes called *tritylene ;* buty- *tetrylene ; caproylene, hexylene ;* &c.

multiple of that of methylene (C_2H_2) by 16, so, allowing for er
experiment, the vapour density of cetylene (8·007) is 16 times th
methylene (0·490).

379. ALCOHOL may be studied as the type of the class to wh
gives a name.

When any of the fermented or distilled liquors of commerce ar
jected to distillation, the alcohol passes over during the first part
process, mixed with a considerable quantity of water; and if the di
tion be continued as long as any alcohol passes over, and the whole
distilled liquid be measured or weighed, the quantity of alcohol p
in the original liquid subjected to distillation, may be inferred (by
ence to a table) from the specific gravity of the aqueous spirit di
from it, since the lighter it is the more alcohol it contains, the
gravity of pure alcohol being 0·794.

The strength of the spirit of wine of commerce is ascertained by
mining its specific gravity. That known as *proof spirit* has the
gravity 0·920, and is so called because it is the weakest spirit whi
answer to the rough proof of firing gunpowder which has been mo
with it and kindled. Any spirit weaker than this leaves the
moist, and does not explode it. It is then said to be *under proof*;
a stronger spirit is spoken of as *over proof*.

Proof spirit contains by weight, in 100 parts—

Water,	.	.	50·76
Alcohol,	.	.	49·24

A spirit would be spoken of as 30 per cent., for example, ove
if 100 measures of it, when diluted with water, would yield 130
of proof spirit. A spirit 30 per cent. *below proof* contains, in e
measures, 70 measures of proof spirit. By repeatedly rectifyin
distilling the weak spirit obtained from a fermented liquid, colle
first portions separately, a strong spirit may be obtained, conta
per cent. of alcohol, but mere distillation will not effect a furth
tion of the water. Weak spirit may be concentrated to a great
than this, by leaving it enclosed in a bladder for a considerabl
when the water exudes through the bladder more readily than th
so that the latter accumulates in the mixture to the amount
cent.

Another method of separating a great part of the water consis
ing dry carbonate of potash to the weak spirit as long as it is
when the mixture separates into two layers, the lower consisting
tion of carbonate of potash in water, and the upper one of spirit
ing 89 per cent. of alcohol. By effecting the separation by mea
bonate of potash in a graduated tube, this method is sometimes
for roughly ascertaining the proportion of alcohol in a ferm
distilled liquid, the foreign matters in which prevent any safe
from the specific gravity.

The last portions of water are removed from alcohol by allow
stand for two or three days over powdered quick-lime, and distill
the lime retains the water in the form of hydrate of lime, and th
absolute alcohol distils over. It must then be preserved in wel
bottles, since it readily absorbs moisture from the atmosphere.
n for water causes it to evolve heat when mixed with that

lume of the mixture is less than the sum of the volumes of its nents, showing that combination has taken place.

. ETHER, or, as it is sometimes erroneously called, *sulphuric ether*), is obtained by distilling a mixture of two measures of alcohol ne measure of concentrated sulphuric acid. As soon as the mixture to blacken, in consequence of a secondary decomposition of the l, the retort is allowed to cool, another half measure of alcohol is , and the mixture again distilled as long as ether is obtained.
ar better method of obtaining ether is that known as the *continuous* s. Alcohol of sp. gr. 0·830 is mixed with an equal measure of con- ted sulphuric acid, and introduced into a retort or flask (fig. 275),

Fig. 275.—Continuous etherification.

is connected with a small cistern containing alcohol. The mixture flask is rapidly raised to the boiling point, and alcohol is allowed to lowly in from the reservoir through a syphon furnished with a stop- so as to keep the liquid in the flask at a constant level. A thermo- should be immersed in the liquid, the temperature of which should intained at 284° to 290° F. By this process, one measure of sul- acid will effect the conversion into ether of thirty measures of l.
boiling point of ether being very low (94°·8 F.) necessitates the yment of a good condensing arrangement in this process.
liquid which distils over contains about two-thirds of its weight er, with about one-sixth of water, and an equal quantity of alcohol. of sulphurous acid are also generally present. To obtain the pure it is shaken with water containing a little carbonate of potash, when ater dissolves the alcohol, and the potash removes the sulphurous the ether being very sparingly soluble in, and much lighter than (sp. gr. 0·74), rises to the surface, holding a little water in solution. pper layer is drawn off and freed from water by distillation in a bath, at a very low heat, over quick-lime.
explanation of the chemistry of this process of *etherification* will re intelligible after some other changes to which alcohol is liable *een studied.*

The most striking properties of ether are its peculiar odour and its great volatility; its rapid evaporation when poured upon the hand gives rise to a sensation of intense cold; and if a little ether be evaporated by blowing upon it in a watch-glass with a drop of water hanging from its convexity, the water will be speedily frozen. Ether is also exceedingly inflammable; and since its vapour is very heavy (sp. gr. 2·59), and passes in an unbroken stream through the air for a considerable distance, great care should be taken to avoid pouring it from a bottle in the neighbourhood of a flame. Its flame is far more luminous than that of alcohol, and much acetylene is produced during its imperfect combustion (p. 85).

The high specific gravity, volatility, and inflammability of ether vapour admit of illustration by some curious experiments:—

If a small piece of sponge be saturated with ether and placed in the centre of a large wooden tray, two or three inches deep, the latter will soon be entirely filled with the vapour, as may be shown by applying a lighted match to one corner. A jug may be warmed by rinsing a little hot water round it, and this having been thrown out, a few drachms of ether may be poured into the jug, which will immediately become filled with ether vapour, and from this several glasses may be filled in succession, the presence of the ether vapour being proved by a lighted taper.

A pneumatic trough may be filled with warm water, a small test-tube filled with ether inverted with its mouth under the water, and the ether quickly decanted up into a gas-jar also filled with hot water, where it will be immediately converted into vapour, and may be decanted through the water into other vessels, and dealt with like a permanent gas. Some cold water poured over the jar containing it at once proves its condensible character.

When ether is acted upon by hydrochloric, hydrobromic, or hydriodic acid, the oxygen of the ether enters into combination with the hydrogen of the acid, and the chlorine, bromine, or iodine, occupies its place.

Thus, with hydrochloric acid—

$$\underset{\text{Ether.}}{C_4H_5O} + HCl = \underset{\substack{\text{Hydrochloric}\\ \text{ether.}}}{C_4H_5Cl} + HO.$$

In a similar manner, *hydrobromic ether*, C_4H_5Br, and *hydriodic ether*, C_4H_5I, may be formed. The best method of obtaining the two last, however, consists in distilling moderately strong alcohol with phosphorus, and either bromine or iodine, when *phosphovinic* or *phosphethylic* acid and hydriodic ether are formed—

$$\underset{\text{Alcohol.}}{6C_4H_6O_2} + P + I_5 = 5C_4H_5I + \underset{\text{Phosphovinic acid.}}{2HO.C_4H_5O.PO_5} + 4HO.$$

These three ethers are colourless fragrant volatile liquids, which are of the greatest value in the investigation of the constitution of compound organic compounds.

This remark applies particularly to hydriodic ether (*iodide of ethyle*), which is less volatile than the others, and therefore more easily manageable in experiments requiring a high temperature.

Iodide of ethyle, or *ethylic iodide*, is prepared by distilling 1400 grains of ordinary alcohol (sp. gr. 0·84) with 2000 grains of iodine, and 100 grains of ordinary vitreous phosphorus. The iodine and phosphorus are added alternately, in small portions

* If alcohol be written $C_4H_5O.HO$, it will be seen that this change is precisely similar to that which occurs in the preparation of hydriodic acid by the simultaneous action of phosphorus and iodine upon water:—

$$6[(C_4H_5)O.HO] + P + I_5 = 5(C_4H_5)I + (C_4H_5)O.2HO.PO_5 + 4HO$$
$$6(HO.HO) + P + I_5 = 5HI + HO.2HO.PO_5 + 4HO.$$

alcohol in the retort, which is immersed in cold water to moderate the action, occasionally shaken. When the whole has been added, the retort is connected a Liebig's condenser, and heated in the water-bath, when about 2½ measured es of iodide of ethyle mixed with alcohol will pass over. This is shaken in a ered bottle with about an equal measure of water, which dissolves the alcohol, ng the iodide of ethyle to collect at the bottom as an oily layer (sp. gr. 1·97). as much as possible of the upper aqueous layer has been removed with a n or pipette, the iodide is poured into a small retort containing fused chloride cium in powder to remove the water. The retort is closed with a cork, and ide for some hours, when the iodide of ethyle may be distilled off in the water- and condensed in a Liebig's condenser.

1. Alcohol-radicals.—If ethylic iodide be poured over granulated contained in a stout glass tube, which is then exhausted of air, hermey sealed, and heated for two hours in an oil-bath to 300° F., a crysne substance is deposited which is a compound of iodide of zinc with thyle (C_4H_5Zn), whilst a colourless liquid separates, consisting nixture of three hydrocarbons, which have been liquefied by their own ure. On breaking the extremity of the tube under water, this liquid lly escapes in the form of gas, which proves on examination to contain nt gas (C_4H_4), hydride of ethyle (C_4H_6), and ethyle (C_4H_5), the last hich may be obtained nearly pure by collecting the last portions of eparately, since ethyle is the least volatile of these hydrocarbons.

eglecting the secondary decompositions which give rise to the other ucts, the formation of ethyle would be represented by the simple tion—

$$\underset{\text{Ethylic iodide.}}{C_4H_5I} + Zn = ZnI + \underset{\text{Ethyle.}}{C_4H_5}.$$

thyle is a colourless gas, having a faint ethereal smell, insoluble in r, and requiring a pressure of two or three atmospheres for its efaction. The interest which attaches to it is due to its being regarded nany chemists as the radical or starting-point of the series of comnds derived from vinic alcohol, which is thence spoken of as the le series, and this view of the constitution of those compounds was vour long before the compound C_4H_5 was obtained in the separate , this being a discovery of very recent date.

[ention has already been made of the existence of another radical hyle (C_2H_3) obtained by a similar process, which may be regarded as starting-point of the wood-spirit series.

utyle (C_8H_9), *amyle* ($C_{10}H_{11}$), and *caproyle* ($C_{12}H_{13}$), the supposed cals of the butylic, amylic, and caproic alcohols, have also been obed, these being liquids with progressive boiling points. We are thus ossession of several members of a homologous series of hydrocarbons, h may be designated the *alcohol-radicals*, and represented by the ral formula, $C_{2n}H_{2n+1}$.

will be evident that the series of aldehydes ($C_{2n}H_{2n}O_2$) and of acids ($C_{2n}H_{2n}O_4$), ed from the alcohols ($C_{2n}H_{2n+2}O_2$), may be regarded as the hydrated oxides of radicals ($C_{2n}H_{2n-1}$) which resemble the non-metallic or electro-negative bodies r than the metals, by their disposition to yield acid rather than basic substances oxidised. Thus, in the series derived from common alcohol—

$$\underset{\text{Aldehyde.}}{C_4H_4O_2} = \underset{\text{Hydrated oxide of } acetyle.}{(C_4H_3)O.HO.}$$

$$\underset{\text{Acetic acid.}}{C_4H_4O_4} = \underset{\text{Hydrated teroxide of } acetyle.}{(C_4H_3)O_3.HO}$$

We should thus have corresponding series of *electro-positive* and *electro-negative radicals*—

Electro-positive radicals. $C_{2n}H_{2n+1}$		Electro-negative radicals. $C_{2n}H_{2n-1}$	
Methyle,	C_2H_3	Formyle,	C_2H?
Ethyle,	C_4H_5	Acetyle,	C_4H_3
Propyle,	C_6H_7	Propionyle,	C_6H_5
Butyle,	C_8H_9	Butyryle,	C_8H_7
Amyle,	$C_{10}H_{11}$	Valeryle,	$C_{10}H_9$
&c.		&c.	

The electro-negative radicals have not been obtained in the separate state.

382. The formulæ above given for the alcohol-radicals represent each equivalent* as yielding only two volumes of vapour (O = 1 vol.), in which respect they would form exceptions to the rule which holds good with all other compounds of carbon and hydrogen, viz., that one equivalent in the state of vapour occupies four volumes (p. 460).†

This anomaly would disappear if the formulæ were doubled, so that ethyle became C_8H_{10}, amyle $C_{20}H_{22}$, and so on. Experiment has shown that these formulæ really must be doubled in order to express correctly the constitution of the hydrocarbons; for if a mixture of iodide of ethyle and iodide of amyle ($C_{10}H_{11}I$, prepared from fousel oil just as iodide of ethyle is from alcohol) be heated with sodium, a colourless liquid is obtained, which is a true combination of ethyle and amyle ($C_4H_5 . C_{10}H_{11}$)

$$\underset{\text{Iodide of ethyle.}}{C_4H_5I} + \underset{\text{Iodide of amyle.}}{C_{10}H_{11}I} + Na_2 = 2NaI + \underset{\text{Ethyle-amyle.}}{C_4H_5 . C_{10}H_{11}}$$

In a similar manner, ethyle-butyle ($C_4H_5 . C_8H_9$), methyle-propyle ($C_2H_3 . C_{12}H_{13}$), butyle-amyle ($C_8H_9 . C_{10}H_{11}$), and butyle-caproyle ($C_8H_9 . C_{12}H_{13}$), have been obtained.

These double radicals all yield four volumes of vapour for each equivalent of the compound,‡ showing that the ordinary formula for methyle (which furnishes only two volumes, must be converted into that of a double radical, methyle-methyle ($C_2H_3 . C_2H_3$), which would give four volumes of vapour, and in a similar manner, ethyle would become ($C_4H_5 . C_4H_5$), ($C_8H_9 . C_8H_9$), and so on.

This duplicate nature of the radicals at once explains the circumstance that they do not unite directly with chlorine, bromine, &c., as might have been expected. Thus ethyle, with iodine, does not combine to form iodide of ethyle, because the ethyle itself is an ethylide of ethyle.

Again, the formation of zinc ethyle (C_4H_5Zn), and of hydride of ethyle (C_4H_5H), during the action of zinc upon iodide of ethyle, becomes intelligible upon this view. Indeed, the first stage of this action appears to consist in the formation of zinc-ethyle—

$$\underset{\text{Iodide of ethyle.}}{C_4H_5I} + Zn_2 = \underset{\text{Zinc-ethyle.}}{C_4H_5Zn} + ZnI .$$

In the second stage, the zinc-ethyle acts upon a fresh portion of iodide of ethyle, producing iodide of zinc and the double radical ethyle—

$$\underset{\text{Iodide of ethyle.}}{C_4H_5I} + \underset{\text{Zinc-ethyle.}}{C_4H_5Zn} = ZnI + \underset{\text{Ethyle.}}{C_4H_5 . C_4H_5} .$$

* Or each molecule as yielding one volume of vapour (H = 1 vol.)

† Or one molecule in the state of vapour occupies 2 vols. (H = 1 vol.)

‡ Or one molecule yields two volumes of vapour (H = 1 vol.)

ydride of ethyle itself clearly corresponds to the double radical one-half of which is replaced by an equivalent of hydrogen H), itself occupying two volumes, like the compound C_4H_5 which displaced.

simultaneous formation of hydride of ethyle and of olefiant gas the action of zinc upon iodide of ethyle, might be represented by quation—

$$\underset{\text{Iodide of ethyle.}}{2C_4H_5I} + Zn_2 = 2ZnI + \underset{\text{Hydride of ethyle.}}{C_4H_5.H} + C_4H_4.$$

ydride of ethyle is the representative of a series of homologous hydro-ns, of which the first member, the hydride of methyle ($C_2H_3.H$), is ical with marsh-gas.

e following table exhibits some of the chief members of the marsh-series of hydrocarbons (general formula $C_{2n}H_{2n+2}$), as well as the cor-onding alcohol radicals,* general formula $2(C_{2n}H_{2n+1})$—

	Radical.	Hydride.†
Methyle, . .	$C_2H_3 . C_2H_3$	$C_2H_3 . H = C_2H_4$
Ethyle, . . .	$C_4H_5 . C_4H_5$	$C_4H_5 . H = C_4H_6$
Butyle, . . .	$C_8H_9 . C_8H_9$	$C_8H_9 . H = C_8H_{10}$
Amyle, . . .	$C_{10}H_{11} . C_{10}H_{11}$	$C_{10}H_{11} . H = C_{10}H_{12}$

The three first of these hydrides are gaseous, the last a volatile liquid.

If ethyle ($C_4H_5 = E$) be accepted as the radical of the alcohol series, en ether (C_4H_5O) would become the oxide of ethyle, and alcohol $C_4H_6O_2 = C_4H_5O . HO$), the hydrated oxide of ethyle; and it will be en that upon this view a considerable number of the relations of these dies can be readily explained.

383. On referring to the action of hydrochloric acid upon ether, it will seen to resemble exactly that of the same acid upon the basic oxide of metal, consisting in an exchange between the chlorine of the acid and e oxygen of the base. Chloride of ethyle may also be produced by the tion of hydrochloric acid upon alcohol (EO . HO), just as chloride of tassium is produced by the action of that acid upon hydrate of tash—

$$\underset{\text{Alcohol.}}{EO.HO} + HCl = \underset{\text{Chloride of ethyle.}}{ECl} + 2HO.$$

It would be expected that the action of other acids upon alcohol would rrespond to their action upon hydrate of potash, and with several acids is is really the case, although it is far more difficult to break up the cohol than the hydrate of potash.

If alcohol be boiled for many hours with dry oxalic acid ($HO . C_2O_3$) in flask provided with a long tube, so that the volatilised alcohol may run ack, it is found that, on diluting the solution with water, a heavy fra-rant liquid separates, which has the composition $C_4H_5O . C_2O_3$, and is rmed *oxalic ether*.

Its formation may be thus represented—

$$\underset{\text{Alcohol.}}{EO.HO} + \underset{\text{Oxalic acid.}}{HO.C_2O_3} = \underset{\text{Oxalic ether.}}{EO.C_2O_3} + 2HO.$$

* See also American petroleum, p. 468.

† Each of these hydrides is isomeric with the radical immediately preceding it. Thu ydride of ethyle has the same composition as methyle, and is regarded by some chemists *entical with it.*

It is formed far more easily in the presence of strong sulphuric acid, since this developes the ether (EO) to combine with the oxalic acid.

By treatment with hydrate of potash, the oxalic ether is decomposed, yielding oxalate of potash and alcohol; thus—

$$EO.C_2O_3 + KO.HO = KO.C_2O_3 + EO.HO.$$

But if the oxalic ether be mixed with only half the quantity of hydrate of potash required for this decomposition, there is obtained, instead of oxalate of potash, a salt, crystallising in pearly scales, having the composition $KO.EO.2(C_2O_3)$, the formation of which is easily understood—

$$\underset{\text{Oxalic ether.}}{2(EO.C_2O_3)} + KO.HO = \underset{\text{Oxalovinate of potash.}}{KO.EO.2C_2O_3} + EO.HO.$$

By decomposing this salt with hydrofluosilicic acid (*see* p. 181) to remove the potassium in an insoluble form, a new acid is obtained, which has the composition $HO.EO.2C_2O_3$, and is called *oxalovinic* or *oxalethylic acid*. It might evidently be also called the binoxalate of oxide of ethyle, since it corresponds in composition to the binoxalate of potash, $KO.HO.2C_2O_3$.

Most of the acids form, with oxide of ethyle, compounds corresponding to oxalic ether; thus, by distilling acetic acid with alcohol and sulphuric acid, and diluting the distilled liquid with water, *acetic ether* ($EO.C_4H_3O_3$) is separated, remarkable for its very fragrant odour, which has a share in the perfume of cider, perry, vinegar, and of many wines.

The ether used in medicine under the names of *sweet spirits of nitre*, *nitrous ether*, and *nitric ether*, is essentially a solution of nitrous ether ($C_4H_5O.NO_3$) in alcohol, and is prepared by distilling alcohol with nitric acid, when a violent and complicated reaction takes place, one portion of the alcohol being converted into aldehyde, at the expense of a part of the oxygen of the nitric acid—

$$\underset{\text{Alcohol.}}{2(C_4H_6O_2)} + HO.NO_5 = \underset{\text{Aldehyde.}}{C_4H_4O_2} + \underset{\text{Nitrous ether.}}{C_4H_5O.NO_3} + 4HO.$$

Nitrous ether is a very volatile liquid, characterised by a powerful odour of rennet-apples, and in the pure state decomposes spontaneously, evolving nitric oxide.

True *nitric ether* ($EO.NO_5$) may also be obtained as a fragrant, heavy oily liquid by distilling alcohol with nitric acid, under certain precautions. It is decomposed with explosion at a temperature of about 200° F.

By the action of nascent hydrogen upon nitric ether, a basic substance is produced which has been named *hydroxylamine*, in allusion to its remarkable formula, NH_3O_2, which might be regarded as ammonia, NH_3, in which one equivalent of hydrogen is replaced by *hydroxyle*, HO_2—

$$\underset{\text{Nitric ether.}}{C_4H_5O.NO_5} + H_6 = \underset{\text{Alcohol.}}{C_4H_5O.HO} + 2HO + \underset{\text{Hydroxylamine.}}{NH_3O_2}.$$

In order to obtain this base, 5 parts of nitric ether are acted on by 12 parts of tin and 50 parts of concentrated hydrochloric acid. When the action is over, the alcohol is expelled by heat, the tin precipitated by hydrosulphuric acid, the solution evaporated to dryness, and the residue boiled with absolute alcohol, which leaves somehydrochlorate of ammonia undissolved. The *hydrochlorate of hydroxylamine* ($NH_3O_2.HCl$) crystallises in long needles from the alcoholic solution. From the sulphate of hydroxylamine, by decomposition with baryta, a solution of the base itself may be obtained, but pure hydroxylamine has not been isolated from the solution, since it has a tendency to decompose into ammonia, water, and nitrogen—

$$\underset{\text{Hydroxylamine.}}{3NH_3O_2} = NH_3 + N_2 + 6HO.$$

The *chloric ether* used for medicinal purposes is not an ether in the true sense

term, but a solution of chloroform (C_2HCl_3) in alcohol. Chloroform will be more particularly described hereafter.

Perchloric ether ($C_4H_5O.ClO_7$) is only interesting from the circumstance that, though an oily liquid, it explodes violently under a sudden blow.

Boracic ether, which has the remarkable formula ($3EO.BO_3$), is formed when terchloride of boron is decomposed by alcohol—

$$BCl_3 + 3(EO.HO) = 3EO.BO_3 + 3HCl$$

It may also be obtained by heating anhydrous boracic acid with an excess of alcohol under pressure. It is lighter than water (sp. gr. 0·88), and boils at 246° F. When heated with anhydrous boracic acid, it is converted into $EO.BO_3$, which is decomposed by heat into $3EO.BO_3$ and $EO.3BO_3$, the latter being a vitreous solid. When bichloride of silicon is decomposed by alcohol, the compound $2EO.SiO_2$ is produced—

$$SiCl_2 + 2(EO.HO) = \underset{\text{Silicic ether.}}{2EO.SiO_2} + 2HCl.$$

This *silicic ether* is a colourless liquid, of sp. gr. 0·93, and distilling unchanged at 320° F. It has an ethereal odour, and burns with a brilliant flame which deposits silica. When poured upon the surface of water, it gradually decomposes, with separation of gelatinous hydrated silica—

$$2EO.SiO_2 + 2HO = 2(EO.HO) + SiO_2.$$
$$\text{Alcohol.}$$

When the ether is kept in a moist atmosphere, it deposits a hard transparent mass of silica, known as *artificial quartz*.

Two other silicic ethers have been obtained, having respectively the composition $EO.SiO_2$ and $EO.2SiO_2$; the former liquid, the latter viscous.

Carbonic ether ($EO.CO_2$) may be obtained by heating carbonate of silver with iodide of ethyle in a sealed tube;

$$AgO.CO_2 + EI = EO.CO_2 + AgI.$$

The compound $2EO.CO_2$ has been obtained by the action of sodium upon an alcoholic solution of chloropicrine—

$$\underset{\text{Chloropicrine.}}{C_2Cl_3(NO_4)} + \underset{\text{Alcohol.}}{4(EO.HO)} + Na_4 = 3NaCl + NaO.NO_3 + \underset{\text{Subcarbonate of ethyle.}}{2(2EO.CO_2)} + H_4.$$

When carbonic acid is passed through a solution of hydrate of potash in absolute alcohol, the *carbovinate of potash* is obtained, in crystals having the composition $KO.EO.2CO_2$, corresponding to bicarbonate of potash, $KO.HO.2CO_2$.

By the action of syrupy phosphoric acid upon alcohol, the compound $2HO.EO.PO_5$, *phosphovinic acid*, is formed, and by neutralising it with a base, a *phosphovinate* may be obtained, composed after the general formula $2MO.EO.PO_5$.

A second acid is formed at the same time, having the formula $HO.2EO.PO_5$, its salts being $MO.2EO.PO_5$. Phosphovinic acid is found abundantly in the residue from the preparation of iodide of ethyle.

The true phosphoric ether ($3EO.PO_5$) is also said to have been obtained.

The true *sulphuric ether* ($EO.SO_3$) can only be formed by passing the vapour of anhydrous sulphuric acid into ether. It is an oily liquid, heavier than water, and decomposed by heat, olefiant gas and alcohol being found amongst the products, for $C_4H_4 + C_4H_6O_2 = 2(C_4H_5O)$.

The fragrant liquid known as *heavy oil of wine*, which is formed towards the latter part of the preparation of ether and of olefiant gas (page 85), appears to contain the sulphate of oxide of ethyle, together with some hydrocarbons of the olefiant gas series. When decomposed with a solution of potash, *light oil of wine* rises, which contains hydrocarbons of the olefiant gas series.

384. When ether or alcohol is added to concentrated sulphuric acid, much heat is evolved, in consequence of the combination of the oxide of ethyle with sulphuric acid, to form *sulphovinic* or *sulphethylic acid*, $HO.EO.2SO_3$ or bisulphate of oxide of ethyle, corresponding in composition to the bisulphate of potash, $KO.HO.2SO_3$. If baryta be now *added to the solution, the* uncombined sulphuric acid will be precipitated

in the form of sulphate of baryta, but the sulphovinic acid will combine with the base to form the sulphovinate of baryta, which may be obtained by evaporating the solution, in rhombic prisms which have the formula $BaO.EO.2SO_3.2Aq.$, and are easily soluble in water. By cautiously adding sulphuric acid to the solution of sulphovinate of baryta till the whole of the baryta is precipitated as sulphate, and evaporating the filtered liquid *in vacuo*, the pure sulphovinic acid is obtained as a syrupy liquor liable to spontaneous decomposition, and readily decomposed when heated with water, into alcohol and sulphuric acid—

$$\underset{\text{Sulphovinic acid.}}{HO.EO.2SO_3} + 2HO = 2(HO.SO_3) + \underset{\text{Alcohol.}}{EO.HO.}$$

385. *Vinic acids are not formed by monobasic acids.*—It must be noticed that although the greater number of the acids are capable of forming ethers only a few of them produce vinic acids. Indeed, only those acids form vinic acids which there is reason to believe are polybasic, *i.e.*, require more than one equivalent of a base for the formation of a neutral salt (p. 2). Thus, sulphuric acid should probably be represented by the formula $2HO.S_2O_6$ instead of by $HO.SO_3$; when sulphate of potash would be $2KO.S_2O_6$, bisulphate of potash $KO.HO.S_2O_6$, and sulphovinic acid $EO.HO.S_2O_6$, the tendency to form a vinic acid depending upon the possibility of replacing a portion of the water of hydration in the acid by oxide of ethyle. In the case of nitric acid, which is undoubtedly a monobasic acid, and does not form acid salts, no vinic acid can be produced, the formula of the acid being $HO.NO_5$, the water of hydration must be *entirely* or not at all replaced by the oxide of ethyle.

386. *Theory of etherification.*—When sulphovinic acid is decomposed by heat, especially in the presence of excess of alcohol, a large product of ether is found among the products, and this has given rise to the general opinion with chemists, that the production of sulphovinic acid is an intermediate stage in the formation of ether, by the ordinary process of distilling alcohol with sulphuric acid. At first sight it would appear that the etherification of alcohol in this process was sufficiently explained by reference to the attraction of sulphuric acid for water, and consists in a simple removal of water from the alcohol by the acid, for—

$$\underset{\text{Alcohol.}}{C_4H_6O_2} - HO = \underset{\text{Ether.}}{C_4H_5O}.$$

When it is found, however, that a continuous stream of alcohol, passing into heated sulphuric acid in a retort, is converted into ether and water, which is not retained by the sulphuric acid, but distils over with the ether, and that this may go on almost without limit, this explanation is no longer tenable.

Accordingly, the formation of ether from alcohol by the action of sulphuric acid is generally referred to the formation of sulphovinic acid, as soon as the alcohol and the acid are brought in contact, and the subsequent decomposition of this sulphovinic acid, in the presence of water or alcohol, into hydrated sulphuric acid, water, and ether; thus—

$$\underset{\text{Sulphovinic acid.}}{HO.EO.2SO_3} + HO = 2(HO.SO_3) + \underset{\text{Ether.}}{EO}, \text{ or}$$

$$\underset{\text{Sulphovinic acid.}}{HO.EO.2SO_3} + \underset{\text{Alcohol.}}{EO.HO} = 2(HO.SO_3) + \underset{\text{Ether.}}{2EO}$$

e hydrated sulphuric acid thus set free would of course give rise to ormation of a fresh quantity of sulphovinic acid, which would be posed in its turn, and so on without limit.

strong argument in favour of this view is deducible from the follow- xperiment:—

hen amylic alcohol (the hydrated oxide of amyle, $C_{10}H_{11}O.HO$) is d with concentrated sulphuric acid, it forms sulphamylic acid $_{11}O.HO.2SO_3$), corresponding to sulphovinic acid, and if this be d in a retort, and alcohol be allowed to flow into it, as in making , the first portion which distils over is found to be a true *double* , composed of one equivalent of ethylic, and one equivalent of amylic ($C_4H_5O.C_{10}H_{11}O$), the production of which would be represented he equation—

$$\underset{\text{Sulphamylic acid.}}{.C_{10}H_{11}O.2SO_3} + \underset{\text{Alcohol.}}{C_4H_5O.HO} = \underset{\text{Amylethylic ether.}}{C_4H_5O.C_{10}H_{11}O} + 2(HO.SO_3).$$

continuing the distillation, nothing but ordinary ethylic ether is ined.

he existence of these double ethers might have been anticipated from t has been said with respect to the double radicals (p. 520), but the le of formation in the above instance certainly affords support to the , that ether results from the decomposition of sulphovinic acid by hol in the ordinary etherifying process.

n the other hand, this theory of etherification is shaken by the cir- stance, that if vapour of alcohol be passed into boiling sulphuric acid, . gr. 1·52 (boiling at 290°), almost the whole of the alcohol is resolved water and ether, which distil over, so that either no sulphovinic acid rmed, or it is only formed to be immediately decomposed. If the acid the sp. gr. 1·61 (boiling at 330°), no ether is obtained, the alcohol g resolved into olefiant gas and water.

oreover, hydrated phosphoric acid cannot be substituted for the sul- ric acid in the preparation of ether, notwithstanding that it also forms nic acid.

ence, many chemists are inclined to attribute to sulphuric acid a ific action by contact (*catalytic action*) upon alcohol, causing its resolu- into water and ether, or olefiant gas, according to the temperature.

his view receives some confirmation from the behaviour of sulphuric towards cellulose and certain other substances, in which it causes ortant transformations, without itself appearing to take part in the ge.

a connection with this subject, it is remarkably interesting to observe, alcohol may actually be reproduced from olefiant gas and water under influence of sulphuric acid. If concentrated sulphuric acid be vio- ly agitated in a vessel containing olefiant gas, the latter is absorbed, on diluting the acid with water and distilling, a quantity of alcohol tained.

his observation of modern date is in favour of the opinion, long since ntained by many chemists, that olefiant gas, and the hydrocarbons ologous with it, should really be regarded as the radicals of the various hols and their derivatives. Upon this view, ether would become the *rate of ethylene* ($C_4H_4.HO$), alcohol would be the *bi-hydrate of ethy- ($C_4H_4.2HO$), &c.*

387. But there are some other facts which conduct us to another opi with respect to the constitution of ether and alcohol.

When potassium or sodium is thrown into absolute alcohol, the m is dissolved with disengagement of heat and rapid evolution of hydr and a crystalline compound is formed, known as *potassium-alcohol* (*late of potash*) or *sodium-alcohol* (*ethylate of soda*), and contains equivalent of the metal in the place of an equivalent of hydrogen action of potassium upon alcohol would be thus represented—

$$\underset{\text{Alcohol.}}{C_4H_5O.HO} + K = \underset{\text{Potassium-alcohol.}}{C_4H_5O.KO} + H.$$

Other alcohols behave in a similar manner. No one can fail to be with the similarity which exists between the action of potassium alcohol and upon water, and chemists have naturally endeavoured t both actions to a common type. This may be done without differ it be borne in mind that the actual result of the decomposition of by potassium is not potash, KO, but hydrate of potash, KO.HO, may with great propriety be regarded as a double equivalent of w which half the hydrogen has been displaced by potassium, KHO_2.

The decomposition of water by potassium would then be repr by the equation—

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O_2 + K = \left.\begin{matrix}K\\H\end{matrix}\right\}O_2 + H.$$

Alcohol may be represented with equal fitness, as water in whi the hydrogen is replaced by ethyle (C_4H_5), or EHO_2, and the a potassium upon it may be thus expressed—

$$\left.\begin{matrix}E\\H\end{matrix}\right\}O_2 + K = \underset{\text{Potassium-alcohol.}}{\left.\begin{matrix}E\\K\end{matrix}\right\}O_2} + H.$$

In a similar manner sodium-alcohol would be formed.*

When sodium-alcohol is heated in a sealed tube with the iodid of the alcohol-radicals, the sodium combines with the iodine, w alcohol-radical enters into the place of the sodium, and a double formed.

Thus, if iodide of methyle (C_2H_3I) be decomposed by sodium-

$$C_2H_3I + \underset{\text{Sodium-alcohol.}}{\left.\begin{matrix}E\\Na\end{matrix}\right\}O_2} = NaI + \underset{\textit{Methyl-ethylic ether.}}{\left.\begin{matrix}E\\C_2H_3\end{matrix}\right\}O_2}$$

In a similar manner *amyl-ethylic ether*, $\left.\begin{matrix}E\\C_{10}H_{11}\end{matrix}\right\}O_2$, would be p

Again, if iodide of ethyle be decomposed by sodium-alcohol, ether is obtained, and the action must in consistency be simi plained—

$$C_4H_5I + \underset{\text{Sodium-alcohol.}}{\left.\begin{matrix}C_4H_5\\Na\end{matrix}\right\}O_2} = NaI + \underset{\text{Common ether.}}{\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2}$$

* Thallium-alcohol, $C_4H_5TlO_2$, has also been obtained as a colourless liquid, r its high specific gravity (3·55) and great refractive and dispersive action ray

>m this it would appear that the formula of common ether should be ed, and this would not only be consistent with the duplication of ormula of ethyle (p. 520), but would destroy an existing anomaly, aking the equivalent of ether in the state of vapour to occupy four nes, whereas the formula C_4H_5O corresponds only to two volumes of ur.

cohol and ether would then be constituted upon the same type, that double equivalent of water, and would still bear to each other the relation as exists between hydrate of potash and potash; thus—

Potassium series.		Ethyle series.	
otassium, . .	K	C_4H_5	Ethyle.
ydrate of Potash,	$\left.\begin{matrix}K\\H\end{matrix}\right\}O_2$	$\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2$	Alcohol.
otash, . .	$\left.\begin{matrix}K\\K\end{matrix}\right\}O_2$	$\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2$	Ether.

he *molecular formulæ* are more convenient for exhibiting the relation between r and alcohol, and their derivatives. Thus if a *molecule* (*see* p. 52) or two ns (or volumes) of hydrogen be taken as the type, the derivation of these com-nds from it may be easily traced.

(Atomic weights; $\Theta = 12$, $H = 1$, $\Theta = 16$.
Atomic volumes; $\Theta = 1$ vol. (?), $H = 1$ vol., $\Theta = 1$ vol.)

Molecular formulæ (2 *vols.*)

Hydrogen,	HH	Ethyle,	$\Theta_2H_5.\Theta_2H_5$
Water,	$HH.\Theta$	Ether,	$\Theta_2H_5.\Theta_2H_5.\Theta$
Hydrate of potash,	$KH\Theta$	Ethylate of potash,	$K.\Theta_2H_5.\Theta$
		Alcohol,	$H.\Theta_2H_5.\Theta$
		Methyl-ethylic ether,	$\Theta H_3.\Theta_2H_5.\Theta$
		Ethyl-amyle,	$\Theta_2H_5.\Theta_5H_{11}$

88. Compounds have been obtained corresponding to alcohol and ether, in which place of the oxygen is occupied by sulphur, and which bear the same relation to lrosulphuric acid as alcohol and ether bear to water.

Hydrosulphuric acid,	$\left.\begin{matrix}H\\H\end{matrix}\right\}S_2$		
Hydrosulphuric ether, (sulphide of ethyle),	$\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}S_2$	Sulphide of potassium,	$\left.\begin{matrix}K\\K\end{matrix}\right\}S_2$
Mercaptan,	$\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}S_2$	Hydrosulphate of potassium,	$\left.\begin{matrix}K\\H\end{matrix}\right\}S_2$

All these compounds are distinguished for their powerful odour of garlic. This especially the case with mercaptan, which is notoriously one of the most evil-elling chemical compounds. It is prepared by distilling solution of hydrosulphate potassium (obtained by saturating potash with hydrosulphuric acid) with sulphob-ate of potash, or better, of lime—

$$KO.C_4H_5O.2SO_3 + \left.\begin{matrix}K\\H\end{matrix}\right\}S_2 = \left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}S_2 + 2(KO.SO_2).$$

Sulphovinate of potash. Mercaptan.

Mercaptan is a light, very volatile and inflammable liquid, sparingly soluble in ter. That it is constituted after the type of hydrosulphuric acid is shown by its ion upon metals and their oxides. Potassium acts upon it precisely as it does on alcohol—

$$\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}S_2 + K = \left.\begin{matrix}C_4H_5\\K\end{matrix}\right\}S_2 + H$$

Mercaptan. Mercaptide of potassium or potassium-mercaptan.

Its name was bestowed in allusion to its action upon the oxide of mercury, w it forms a white crystalline inodorous compound, insoluble in water but soluble alcohol—

$$\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}S_2 + HgO = \left.\begin{matrix}C_4H_5\\Hg\end{matrix}\right\}S_2 + HO.$$

Mercaptan. Mercaptide of mercury.

389. *Hydrocyanic ether* ($C_4H_5.C_2N$ = ECy), or cyanide of ethyle, is obtain distilling sulphovinate of potash with cyanide of potassium—

$$KO.EO.2SO_3 + KCy = ECy + 2(KO.SO_3).$$

Sulphovinate of potash. Hydrocyanic ether.

The cyanide of ethyle is a volatile poisonous liquid, smelling strongly of Its most interesting feature is, that when boiled with a solution of potash, it fur propylate of potash, whilst ammonia is evolved—

$$C_4H_5.C_2N + KO.HO + 2HO = KO.C_6H_5O_3 + NH_3.$$

Hydrocyanic ether. Propylate of potash.

In a similar manner, the cyanides of all the alcohol-radicals, when boile solution of potash, yield the potash-salt of the acid which stands next homologous series. Thus cyanide of *methyle* ($C_2H_3.C_2N$) yields the potash acetic acid belonging to the *ethyle* series; cyanide of *amyle* ($C_{10}H_{11}.C_2N$) caproate of potash belonging to the *caproyle* series, and so on. This mode of position argues strongly that hydrogen is really the type of these radicals, fo hydrocyanic acid (HC_2N) is boiled with solution of potash, it yields the pot of formic acid, the lowest member of the homologous series—

$$HC_2N + KO.HO + 2HO = KO.C_2HO_3 + NH_3.$$

Hydrocyanic acid. Formiate of potash.

Thus, leaving the potash out of consideration;

$$H.C_2N + 4HO = C_2H_2O_4 + NH_3$$

Cyanide of hydrogen. Formic acid.

$$C_2H_3.C_2N + 4HO = C_4H_4O_4 + NH_3$$

Cyanide of methyle. Acetic acid.

$$C_4H_5.C_2N + 4HO = C_6H_6O_4 + NH_3.$$

Cyanide of ethyle. Propylic acid.

A plausible explanation of these changes may be given, if the hydrocya (HC_2N) be represented as ammonia (NH_3), in which two equivalents of h are replaced by two equivalents of carbon (just as one equivalent of hyd water is replaced by one equivalent of carbon to form carbonic oxide).

$$N\left\{\begin{matrix}H\\C_2\end{matrix}\right. + \left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_4 = \left.\begin{matrix}H_2\\C_2\end{matrix}\right\}O_4 + N\left\{\begin{matrix}H\\H_2\end{matrix}\right.$$

Hydrocyanic acid. Water. Formic acid. Ammonia.

$$N\left\{\begin{matrix}(C_2H_3)\\C_2\end{matrix}\right. + \left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_4 = \left.\begin{matrix}(C_2H_3)H\\C_2\end{matrix}\right\}O_4 + N\left\{\begin{matrix}H\\H_2\end{matrix}\right.$$

Cyanide of methyle. Acetic acid.

$$N\left\{\begin{matrix}(C_4H_5)\\C_2\end{matrix}\right. + \left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_4 = \left.\begin{matrix}(C_4H_5)H\\C_2\end{matrix}\right\}O_4 + N\left\{\begin{matrix}H\\H_2\end{matrix}\right.$$

Cyanide of ethyle. Propylic acid.

The cyanides of the alcohol radicals will be again referred to under the designation of *nitriles*.

KAKODYLE SERIES—ORGANO-METALLIC BODIES.

. One of the most pleasing results of the progress of investigation mistry, is the discovery of the true position among classified com- s which is to be assigned to some substance hitherto regarded as alous, and as destroying by its presence the symmetry and complete- of an otherwise perfect classification. Such was the case, until the last few years, with *kakodyle*, and the bodies derived from it. vered long before the science of organic chemistry was prepared to e it, it taxed the ingenuity of chemists to find a place for it in their gement of organic compounds, and always occupied an anomalous solated position. Modern research has now brought to light a whole of compounds, which would not have been complete without kako- , and this hitherto incomprehensible substance has at length been ned its proper place.

hen a mixture of equal weights of arsenious acid and dry acetate of sh is submitted to distillation, a heavy poisonous liquid is obtained, h has a most disgusting odour of garlic, and takes fire spontaneously n exposed to the air. This liquid, which has long been known under the es of *alcarsin* (arsenical alcohol), and *Cadet's fuming liquor*, has the position C_4H_6AsO, and its production may be represented (if the us secondary products be neglected) by the equation—

$$\underset{\text{tate of potash.}}{KO.C_4H_3O_3} + AsO_3 = \underset{\text{Alcarsin.}}{C_4H_6AsO} + 2(KO.CO_2) + 2CO_2.$$

acetic acid be represented by the formula derived above (p. 528) from its ation in the action of water upon cyanide of methyle, the formation of alcarsin d be easily explained. Acetate of potash would then be represented by the ula $\left.\begin{matrix}(C_2H_3)K\\C_2\end{matrix}\right\}O_4$, and its action upon arsenious acid might be thus ex- ed—

$$\underset{\text{enious acid.}}{As\left\{\begin{matrix}O\\O_3\end{matrix}\right.} + 2\underset{\text{Acetate of potash.}}{\left(\left.\begin{matrix}(C_2H_3)K\\C_2\end{matrix}\right\}O_4\right)} = \underset{\text{Alcarsin.}}{As\left\{\begin{matrix}O\\(C_2H_3)_2\end{matrix}\right.} + 2(KO.CO_2) + 2CO_2.$$

lcarsin has the properties of a base; it is capable of combining with oxygen acids to form crystallisable salts, and in contact with the ogen acids it furnishes water, together with a salt of the radical of the

Thus, with hydrochloric acid, we have—

$$\underset{\text{Alcarsin.}}{C_4H_6AsO} + HCl = \underset{\text{Chloride.}}{C_4H_6AsCl} + HO.$$

best method of obtaining this chloride consists in dissolving the alcarsin cohol, and adding an alcoholic solution of chloride of mercury, when ite crystalline solid is obtained, composed of $C_4H_6AsO.HgCl$; and istilling this with hydrochloric acid (out of contact with air), another taneously inflammable liquid is obtained, of insupportable odour, and posed of C_4H_6AsCl. By distilling this chloride with zinc in an atmo- re of carbonic acid gas, a third unbearable liquid is procured, which the formula C_4H_6As,* and has been named *kakodyle*, in allusion to

This formula represents only two volumes of vapour for each equivalent. Strictly ing, therefore, it should be doubled (*see* p. 520.)

its intolerable odour (κακός, *bad*). This substance is obviously the ra from which the compounds just mentioned are immediately derived; the

Kakodyle, C_4H_6As = Kd

Alcarsin, or oxide of kakodyle, C_4H_6AsO = KdO

Chloride of kakodyle, C_4H_6AsCl = KdCl.

The remarkable properties of kakodyle leave no doubt as to its really the radical of these compounds, in the same sense in which sium is the radical of the oxide and chloride of that metal, for kak enters into direct combination with chlorine and with oxygen, its attra for the latter being so energetic as to cause its spontaneous inflamm in the air.

The discovery of this radical, comporting itself in all respects metal, was of the utmost importance in its effect upon organic che affording very strong ground for belief in the existence of other metallic radicals, such as ethyle, methyle, &c., which have only n been isolated. A similar service had been previously rendered science by the discovery of the compound radical *cyanogen* (C_2N) b ing to the electro-negative class opposed to the metals, and for a lon these two remained the only compound radicals which had been ob in a separate form.

When kakodyle is brought gradually in contact with oxygen, it converted into the oxide of kakodyle (C_4H_6AsO), and subsequentl *kakodylic acid* ($HO.C_4H_6AsO_2 = HO.KdO_2$), which forms pri crystals, unaltered by air, and destitute of poisonous character. treated with hydrochloric or hydrosulphuric acid, it yields *terc* ($KdCl_3$) and *tersulphide of kakodyle* (KdS_3).

The most poisonous member of this series is the *cyanide of ka* ($C_4H_6As.C_2N$ = KdCy), which is easily obtained in crystals by dec ing cyanide of mercury in solution with oxide of kakodyle—

$$HgCy + KdO = HgO + KdCy.$$

A very minute quantity of this substance diffused in vapour throu air has the most dangerous effect upon those inhaling it.

The following are the most important members of the kakodyle se

Kakodyle,	$C_4H_6As = Kd$
Oxide of kakodyle,	$C_4H_6AsO = KdO$
Sulphate of kakodyle,	$C_4H_6AsO.SO_3 = KdO.SO_3$
Sulphide of kakodyle,	$C_4H_6AsS = KdS$
Chloride of kakodyle,	$C_4H_6AsCl = KdCl$
Kakodylic acid,	$HO.C_4H_6AsO_2 = HO.KdO_2$
Kakodylate of silver,	$AgO.C_4H_6AsO_3 = AgO.KdO_3$
Tersulphide of kakodyle,	$C_4H_6AsS_3 = KdS_3$
Terchloride of kakodyle,	$C_4H_6AsCl_3 = KdCl_3$

391. *Organo-metallic compounds.*—The only way of referring t to any known series was to regard it as an association of arsenic equivalents of methyle (C_2H_3), and this supposition necessit existence of other compounds of a similar nature, formed, that i association of an inorganic element with a quasi-metallic radical. ingly, within the last few years, it has been discovered that b the iodides of methyle, ethyle, and amyle, with zinc, compounds radicals with the metal can be obtained, and these compounds, l yle, are distinguished by their remarkable attraction for oxygen

rsenic and zinc the only elements with which these radicals ociated; boron, potassium, sodium, magnesium, aluminum, in, antimony, bismuth, lead, and mercury may be made to ilar compounds, and the principle is now fully established that radicals can enter into combination with metals to form com- ch are, in some cases, capable of direct union with oxygen and o-negative elements, for which they exhibit a greater attraction etals themselves.

abers of this class of *organo-metallic* bodies which have been s of some of the most important researches deserve special

yle is prepared by the action of zinc upon iodide of ethyle— $In_2 = C_4H_5Zn + ZnI$.

of bright freshly granulated and thoroughly dried zinc are placed in a k (E, fig. 276), which is connected with the carbonic acid apparatus (A),

Fig. 276.—Preparation of zinc-ethyle.

he gas is passed through strong sulphuric acid in the bottles (B and C) oroughly dried. A second perforation in the cork of the flask (E) allows f the tube *f*, which passes through the two corks in the wide tube F, and ttle mercury in D. A stream of cold water is kept running through e (F), being conveyed by the caoutchouc tubes *t t*. When the whole s been filled with carbonic acid, the cork of the flask (E) is removed, and iodide of ethyle (perfectly free from moisture) are introduced, the cork eplaced. The carbonic acid is again passed for a short time, and then osing the nipper-tap (T) upon a caoutchouc connector, when the gas gh the tube (G), which dips into mercury. A gentle heat is then applied ath to the flask (E) till the iodide of ethyle boils briskly, the vapour sed in the tube *f*, and running back into the flask. In about five hours on is complete, and the iodide ceases to distil. The nipper-tap (T) is and a slow current of carbonic acid allowed to pass; the position of r (F) is reversed (fig. 277), and the tube *f* is connected, by the cork K, rt test-tube O; the longer limb of a very narrow syphon (I) of stout through a second perforation in the cork (K), the shorter limb passing short test-tube (P), the cork of which is also furnished with the short erately wide tube (L). For receiving and preserving the zinc-ethyle, a nall tubes are prepared of the form shown in fig. 278. The long narrow one of these is passed down the short tube (L) to the bottom of P, the N) of the tube being connected with an apparatus for passing dry car- *The whole of the apparatus* being filled with this gas, the nipper-tap is

closed, and the flask (E) heated on a sand-bath, so that the zinc-ethyle may over, a slow stream of carbonic acid being constantly passed into P, fr

Fig. 277.—Collection of zinc-ethyle.

escaping through L. When enough zinc-ethyle has collected in the blowpipe flame is applied to the narrow tube (N), which is drawn off a the syphon tube (I) i dually pushed down, longer limb may be suff mersed in the zinc-eth nipper-tap (T, fig. 27 when the pressure of acid forces over a part

Fig. 278

ethyle into the tube P. By heating the tube (M) with a spirit-lamp, s part of the carbonic acid, and allowing it to cool, it will become parti zinc-ethyle, and may be withdrawn and quickly sealed by the blo spontaneous inflammability of the zinc-ethyle, and its easy decompositi render great care necessary in its preparation. If an alloy of zinc wit its weight of sodium be employed, the conversion may be effected in an

If any moisture were present in the materials employed decompose a corresponding quantity of the zinc-ethyle, yieldi zinc and gaseous hydride of ethyle—

$$\underset{\text{Zinc-ethyle.}}{C_4H_5.Zn} + HO = \underset{\text{Hydride of ethyle.}}{C_4H_5.H} + ZnO.$$

Zinc-ethyle is a colourless liquid of powerful odour, heavier (sp. gr. 1·18), and boiling at 244° F. In contact with atmo it takes fire spontaneously, burning with a dazzling greenish- which emits white clouds of oxide of zinc. If a piece of depressed upon the flame, a deposit of metallic zinc is formed, by a ring of oxide, which is yellow while hot, and white on c

When oxygen is allowed to act very gradually upon zinc- alcohol (or ethylate of zinc) is formed, corresponding to po sodium-alcohol (ethylates of potash and soda), which have l described—

$$C_4H_5.Zn + O_2 = \underset{\text{Zinc-alcohol.}}{ZnO.C_4H_5O}.$$

Under the gradual action of other electro-negative element is decomposed into compounds of zinc and ethyle with t element employed; $C_4H_5.Zn + I_2 = C_4H_5I + ZnI$.

Zinc-methyle ($C_2H_3.Zn$) is prepared by the action of zinc up of methyle (C_2H_3I), and resembles zinc-ethyle in its general is, however, far more volatile and more energetic in its re zinc-ethyle, and is decomposed with inflammation and e

contact with water, yielding oxide of zinc and marsh-gas methyle).

$$C_2H_3.Zn + HO = C_2H_3.H + ZnO.$$

Hydride of methyle.

le ($C_{10}H_{11}.Zn$) is not so violent in its reactions; it does not n exposed to air, but absorbs oxygen very rapidly.

n-ethyle and *sodium-ethyle* ($C_4H_5.K$ and $C_4H_5.Na$) have as tained only in combination with zinc-ethyle by heating this sealed tube with potassium or sodium, when metallic zinc is nd the alkali-metal takes its place—

$$H_5.Zn) + Na = 2(C_4H_5.Zn), C_4H_5.Na + Zn.$$

le compound of sodium-ethyle with zinc-ethyle is a crystalline decomposes water with great violence, forming soda, oxide of ydride of ethyle.* Its behaviour with carbonic acid is very nd important.

e crystalline compound of sodium-ethyle with zinc-ethyle is into a bulb-tube through which dry carbonic acid gas is passed, is evolved, zinc-ethyle distils off, and a white solid is left in hich is found to consist of the propylate of soda, $NaO.C_6H_5O_3$, rding to the equation—

$$C_4H_5Na + 2CO_2 = NaO.C_6H_5O_3.$$

tion is one of very great importance, representing the first suc- npt to produce directly one of the organic acids from carbonic dicating a general method for the formation of the other acids series.

odium-methyle be treated in the same way, it yields acetate of

$$C_2H_3Na + 2CO_2 = NaO.C_4H_3O_3.$$

ng iodide of methyle in a sealed tube with a compound of sodium, kakodyle or *arsenio-dimethyle* is obtained—

$$C_2H_3.I) + AsNa_2 = As(C_2H_3)_2 + 2NaI$$

Kakodyle.

kodyle finds its place among the organo-metallic bodies, the which it foreshadowed.

lide of ethyle is treated in a similar manner, *arsenio-diethyle*, r ethyle-kakodyle, is obtained.

enio-trimethyle, or *trimethylarsine*, $As(C_2H_3)_3$, and *arsenio- triethylarsine*, $As(C_4H_5)_3$, may be obtained either by acting lides of methyle and ethyle with a compound of arsenic with lents of sodium—

$$C_2H_3.I) + AsNa_3 = As(C_2H_3)_3 + 3NaI$$

mposing zinc-methyle or zinc-ethyle with terchloride of

$$C_4H_5Zn) + AsCl_3 = As(C_4H_5)_3 + 3ZnCl.$$

thyle has a kakodylic odour, but does not take fire when ex- , although it oxidises with great rapidity. Like kakodyle, it

say, when this compound of sodium-ethyle with zinc-ethyle is heated, it *sodium and zinc.*

is capable of producing a base by combination with oxygen, which has the formula $As(C_4H_5)_4O_2$, and is called *arsenic triethoxide*. Similar compounds have been obtained in which the oxygen is replaced by chlorine, iodine, and sulphur.

Other arsenical compounds of ethyle and methyle have been produced containing four equivalents of the alcohol-radical and one equivalent of an electro-negative element, such as oxygen or iodine, but the oxide of tetrethyl-arsonium, $As(C_4H_5)_4O$, and its congeners are really substances belonging to the ammonium family, and they will be again alluded to elsewhere.

Stibethyle, $Sb(C_4H_5)_3$, or stibiotriethyle, and stibiotrimethyle, $Sb(C_2H_3)_3$, are obtained by processes similar to those which furnish the corresponding compounds of arsenic, which they much resemble.

Stibethyle has a powerful odour of onions, and takes fire spontaneously in air. It combines with two equivalents of oxygen, chlorine, iodine, and sulphur, with great energy. So powerful is its attraction for chlorine, that it displaces hydrogen from concentrated hydrochloric acid—

$$Sb(C_4H_5)_3 + 2HCl = \underset{\text{Bichloride of stibethyle.}}{Sb(C_4H_5)_3 . Cl_2} + H_2.$$

The *binoxide of stibethyle* is a basic substance. The iodide of tetrethylstibonium, $Sb(C_4H_5)_4I$, belongs to the ammonium family.

Mercuric methide ($Hg . C_2H_3$) and *ethide* ($Hg . C_4H_5$) are formed by the action of zinc-methyle and zinc-ethyle upon chloride of mercury—

$$Zn . C_4H_5 + HgCl = ZnCl + Hg . C_4H_5.$$

The methyle compound is the heaviest liquid (except metallic mercury) which is known; its specific gravity is 3·07, so that glass floats upon its surface.

Aluminum ethide, $Al_2(C_4H_5)_3$, is obtained by decomposing mercury ethide with aluminum, $3HgE + Al_2 = Hg_3 + Al_2E_3$. It is a colourless liquid, spontaneously inflammable, and decomposed by water. The corresponding methyle compound, $Al_2(C_2H_3)_3$, solidifies a little above 32° into a transparent crystalline mass.

Triborethyle $B(C_4H_5)_3$, corresponding in composition to boracic ether, BO_3, has been obtained by the action of zinc-ethyle upon boracic ether ($3C_4H_5O . BO_3$)—

$$\underset{\text{Boracic ether.}}{3EO . BO_3} + \underset{\text{Zinc-ethyle.}}{3ZnE} = \underset{\text{Triborethyle.}}{BE_3} + \underset{\text{Ethylate of zinc.}}{3(ZnO . EO)}.$$

It distils over as a very light (sp. gr. 0·69) colourless liquid which has an irritating odour, and is insoluble in water. It inflames spontaneously in air, burning with a beautiful green flame, and explodes when brought in contact with pure oxygen. By gradual oxidation it is converted into the compound BE_3O_4, which may be distilled *in vacuo* without decomposition. When this liquid is mixed with water it is decomposed, forming alcohol, and a volatile white crystalline body, BH_2EO_4—

$$BE_3O_4 + 4HO = BH_2EO_4 + \underset{\text{Alcohol.}}{2(EO . HO)}.$$

This substance has an agreeable odour, and a most intensely sweet taste; it is very soluble in water, alcohol, and ether.

Boric methide, $B(C_2H_3)_3$, is formed by the action of a strong ether solution of zinc-methyle upon boracic ether—

$$\underset{\text{Boracic ether.}}{3EO . BO_3} + \underset{\text{Zinc-methyle.}}{3ZnMe} = \underset{\text{Boric methide.}}{BMe_3} + \underset{\text{Ethylate of zinc.}}{3ZnO . EO}.$$

formation in this manner proves that triborethyle is not a result of re deoxidation of boracic ether, but is produced by the substitu- three equivalents of ethyle for the oxygen in the boracic acid.

ic methide is a heavy (sp. gr. 1·93) colourless gas, having an intoler- ungent tear-exciting odour, and capable of liquefaction under a re of three atmospheres at 50° F. When it issues very slowly into r from a tube, it undergoes partial oxidation, and produces a lam- blue flame, invisible in daylight, and incapable of burning the s; but when it comes rapidly into contact with air, it burns with a t green hot flame, remarkable for the immense quantity of large s of carbon which it disperses through the air, apparently because oracic acid produced envelopes them and prevents their combustion. methide combines with an equal volume of ammonia gas, producing ite, volatile compound $NH_3 . BMe_3$, which is deposited in fine crystals its ethereal solution, and may be sublimed without decomposition. apour, like that of sal-ammoniac, occupies eight volumes instead of . Water absorbs very little boric methide, but alcohol dissolves it ily. Solutions of the alkalies and alkaline earths also absorb it, and sh decomposes the ammonia compound, but the combinations of boric hide with the alkalies do not crystallise, and are decomposed even by onic acid.

ilicium-ethyle, SiE_2, results from the decomposition of bichloride of on with zinc-ethyle; it is not decomposed by water or by solution of sh, is lighter than water, and burns with a bright flame. Silicium- yle is especially interesting as the source of a new alcohol in which a of the carbon appears to be replaced by silicon. The formula of this hol is said to be $Si_2C_{16}H_{20}O_2$, which may be represented as the (miss- *see* p. 512) alcohol $C_{18}H_{20}O_2$ (nonyle-alcohol), in which two equivalents arbon are replaced by two equivalents of silicon.

ilicium-methyle, $Si(C_2H_3)_2$, is obtained by the action of chloride of on upon iodide of methyle in the presence of zinc. It is a liquid ch burns with a luminous flame, producing white fumes of silica.

93. The following table exhibits the composition of the principal com- nds of alcohol-radicals with inorganic elements which have yet been ysed, omitting some of the compound ammonias, which will be noticed after:—

Compounds of alcohol-radicals with inorganic elements.	Equivalent Formula.	Inorganic Type.
Sodium-ethyle,	NaE*	NaO
Magnesium-ethyle,	MgE	MgO
Aluminum-ethyle,	Al_2E_3	Al_2O_3
Zinc-methyle,	$ZnMe$	ZnO
Zinc-ethyle,	ZnE	ZnO
Zinc-amyle,	$ZnAyl$	ZnO
Stan-methyle,	$SnMe$	SnO
Stan-ethyle,	SnE	SnO
Sesquiethide of tin,	Sn_2E_3	Sn_2O_3
Diethiodide of tin,	Sn_2E_2I	Sn_2O_3

Strictly speaking, these formulæ should be doubled, for, as they stand at present, they spond only to two volumes of vapour. Thus sodium-ethyle should be Na_2E_2, and so *xcepting* Al_2E_3, Sn_2E_3, Sn_2E_2I, BiE_3, SbE_3, $AsMe_3$, and their derivatives.

Compounds of alcohol-radicals with inorganic elements.	Equivalent Formula.	Inorganic Type.
Stannic ethide,	SnE_2	SnO_2
Stannic ethylomethide,	$SnEMe$*	SnO_2
Stannic iodethide,	$SnEI$	SnO_2
Bismuthous ethide,	BiE_2	BiO_3
Bismuthous dichlorethide,	$BiECl_2$	BiO_3
Plumbic ethide,	PbE_2	PbO_2
Mercuric ethide,	HgE	HgO
Mercuric methide,	$HgMe$	HgO
Stibethyle,	SbE_3	SbO_3
Antimonic triethoxide,	SbE_3O_2	SbO_5
Iodide of tetrethyl-stibonium,	SbE_4I	SbO_5
Kadodyle,	$AsMe_2$	AsO_3
Oxide of kakodyle,	$AsMe_2O$	AsO_3
Arsenious dioxymethide,	$AsMeO_2$	AsO_3
Trimethyle-arsine,	$AsMe_3$	AsO_3
Monomethyl arsenic acid,	$AsMeO_4$	AsO_5
Kakodylic acid,	$AsMe_2O_2$	AsO_5
Sulphokakodylic acid,	$AsMe_2S_2$	AsO_5
Terchloride of kakodyle,	$AsMe_2Cl_2$	AsO_5
Ethyl-kakodylic acid,	AsE_2O_2	AsO_5
Arsenic triethoxide,	AsE_3O_2	AsO_5
Oxide of tetrethylarsonium,	AsE_4O	AsO_5
Oxide of dimethyl-diethylarsonium,	$AsMe_2E_2O$	AsO_5
Triborethyle,	BE_3	BO_3
Boric methide,	BMe_3	BO_3
Silicium-ethyle,	SiE_4	SiO_2
Silicium-methyle,	$SiMe_4$	SiO_2

These compounds are evidently formed upon the types of the i combinations of the respective elements. Those elements which in only one proportion with oxygen or sulphur, also combine in portion with an alcohol-radical; whilst those which form more compound with oxygen and sulphur also generally form corre compounds with alcohol-radicals.

Thus zinc, which combines with only one equivalent of oxyge phur, also associates itself with one equivalent of methyle, e amyle. Aluminum also combines only in one proportion with th radicals, but that proportion corresponds with the composition of the only oxide of aluminum.

Tin, on the other hand, forms three distinct series of compou the alcohol-radicals, composed according to the types of the p sesquioxide, and binoxide of tin, respectively. And it must be that as long as the type is adhered to, the particular radical occ place in the compound appears to be a matter of indifference; find, in the bodies composed after the type of sesquioxide of tin one in which the places of the three equivalents of oxygen are occ ethyle, and another in which only two of the places are occu ethyle (an electro-positive or quasi-metallic or *basylous* radical), w

* Formed by the action of zinc-methyle upon the stannic iodethide, $SnIEe$. $SnEMe + ZnI$.

d is filled by iodine (an electro-negative or *chlorous* radical). The tin-pounds illustrate peculiarly well the true constitution of these com-ds, for the stan-ethyle and stan-methyle, composed upon the type of nous oxide, exhibit the same tendency which is noticed in that oxide esolve themselves into metallic tin and compounds of the SnO_2 type; s, when stan-ethyle is subjected to distillation $2SnE = SnE_2 + Sn$; as when stannous oxide is boiled with potash, $2SnO = SnO_2 + Sn$.

Among the members of the arsenic series, we have kakodyle composed r the type of realgar, AsS_2, which has no corresponding oxide; then ethylarsine representing arsenious acid, and oxide of tetramethyl-nium ($AsMe_4O$), corresponding to arsenic acid; and just as arsenious is converted into arsenic acid under the influence of oxidising agents, but much more easily, the oxide of kakodyle ($AsMe_2O$), composed n the type AsO_3, is converted into kakodylic acid ($AsMe_2O_3$), repre-ting the type AsO_5. The stability of kakodylic acid necessarily follows n its constitution, the combining tendency of arsenic is saturated in type AsO_5, the force of chemical attraction can go no further.

The discovery of these remarkable compounds draws more closely gether the departments of inorganic and organic chemistry, exhibits a ility of interchange among elementary and compound radicals which s not before suspected, and, whilst helping to establish the doctrine of mpound radicals, teaches that the theory of types must be regarded as e of the most important guides in research.

ORGANIC ALKALOIDS—AMMONIAS.

394. The attraction which the vegetable alkaloids have always possessed r the chemical inquirer is easily accounted for; composing, as they do, so ry small a portion of the plants in which they are found, and yet repre-nting, in many cases, the whole virtue and activity of such plants in eir action upon the animal body, it is very natural that their composi-on should have been very carefully studied, with a view to explain the anges by which they are produced in the plants, and, if possible, to itate those changes in order to obtain these valuable remedies by arti-ial means. In this study, however, the chemist has to contend with fficulties of no insignificant character; for even in the determination of e ultimate composition of these alkaloids, their high equivalent weights d comparatively small proportion of hydrogen render the exact determi-ation of this substance a matter of great difficulty, so that even at the esent time the composition of some of the less known alkaloids can rdly be said to be definitely established.

The following table includes the most important of those alkaloids hich are extracted from plants:—

Alkaloid.	Source.	Equivalent Formula.
Morphine	Opium	$C_{34}H_{19}NO_6$
Codeine	„	$C_{36}H_{21}NO_6$
Narcotine	„	$C_{46}H_{25}NO_{14}$
Papaverine	„	$C_{40}H_{21}NO_8$
Quinine	Cinchona bark	$C_{40}H_{24}N_2O_4$
Cinchonine	„	$C_{40}H_{24}N_2O_2$
Quinidine	„	$C_{40}H_{24}N_2O_4$

Alkaloid.	Source.	Equivalent Form
Caffeine	Coffee	$C_{16}H_{10}N_4O_4$
Theine	Tea	
Theobromine	Cacao-nut	$C_{14}H_8N_4O_4$
Strychnine	Nux vomica	$C_{42}H_{22}N_2O_4$
Brucine	"	$C_{46}H_{26}N_2O_8$
Nicotine	Tobacco	$C_{10}H_7N$
Solanine	Potato-shoots	
Atropine	Deadly nightshade . . .	$C_{34}H_{23}NO_6$
Daturine	Stramonium	
Cocaine	Coca-leaves	$C_{34}H_{21}NO_8$
Hyoscyamine	Henbane, ...	
Emetine	Ipecacuanha	
Aconitine	Aconite	
Veratrine	White hellebore	$C_{64}H_{52}N_2O$
Coniine	Hemlock	$C_{16}H_{15}N$
Piperine	Pepper	$C_{68}H_{28}N_2O$
Capsicine	Cayenne pepper	
Sparteine	Common broom	$C_{16}H_{12}N$
Curarine	Curara poison	$C_{20}H_{14}N$

From this table it is seen that the alkaloids invariably conta and though this element generally forms a comparatively smal weight of the alkaloid, not exceeding 31 per cent. in theobro is the richest in nitrogen, and falling as low as 3·2 per cent. which is the poorest, it is from this element that chemists started in their speculations upon the constitution of these impo

The earliest view of any importance respecting the constit alkaloids was that of Berzelius, who, resting upon the const of nitrogen and hydrogen in these substances, regarded them a of certain neutral substances (then unknown in the separat ammonia, to which they owed their alkaline characters, and was much strengthened when it was discovered that certain (though not those actually found in plants) could be pro direct combination of ammonia with neutral substances ; mustard ($C_8H_5NS_2$), when combined with ammonia (NH_3), y *thiosinnamine* ($C_8H_8N_2S_2$).

To this view it was objected, that ammonia could not b these organic bases, and as the doctrine of the displacement o by another, or by a quasi-element, gained ground, it was s the organic bases might be really constituted in the sam ammonia itself, the place of a portion of the hydrogen being a group composed of carbon and hydrogen, or of carbon, h oxygen. This view of the constitution of the alkaloids, the at once propose ammonia as the type of this large class.

In the earlier attempts to refer the organic bases to amm type, it was said that just as that substance is composed o (one of nitrogen and three of hydrogen), so are the organic b the le contain only two separate hydrogen-atoms, the place atom of that element being occupied by a compound which d functions of that third atom of hydrogen, and does not dest ine character of the original ammonia type.

pply this view to one of the least complex of the organic bases, ($C_{12}H_7N$), we might represent it as ammonia (NH_3), in which the tom of hydrogen had been displaced by the hypothetical compound *phenyle* ($C_{12}H_5$) for $C_{12}H_7N = NH_2 . C_{12}H_5$, *phenylamine*.

view of the constitution of aniline was supported by the fact, that may be obtained by the action of heat upon phenate of ammonia;

$$\underset{\text{Phenate of ammonia.}}{NH_2 . HO . C_{12}H_5O} - 2HO = \underset{\text{Aniline.}}{NH_2 . C_{12}H_5}$$

the substances derived from ammoniacal salts by the loss of two lents of water were called *amides* (being supposed to contain *gen*, NH_2 (*see* p. 239), this theory was spoken of as the *amide-theory* constitution of organic bases.

er research has only extended this theory, having proved that nia is the type of at least the greater number of organic bases, and ot only one, but all three of the hydrogen-atoms, are movable, and e displaced by compound radicals, whilst even the nitrogen of the also admits of replacement by other elements of the same chemical y, viz., by phosphorus, arsenic, and antimony.

more instructive example of the elasticity of a type cannot be given.

5. *Ethylated ammonias and their derivatives.*—When iodide of e (C_4H_5I) is heated in a sealed tube with an alcoholic solution of onia, in the proportion of single equivalents, a crystalline compound med, which might at first be regarded merely as a combination of wo bodies employed to produce it ($C_4H_5I . NH_3$); but when this ance is distilled with potash, it furnishes, instead of ammoniacal gas, our which condenses, under the ordinary pressure in a receiver cooled e, to a very light colourless liquid, which boils at 65°·6 F., and has verful ammoniacal odour. By analysis, this liquid is found to have omposition C_4H_7N, being, in fact, ammonia in which one-third of the ogen has been displaced by ethyle. That this is the true view of its itution does not admit of a doubt, since it so nearly resembles onia in all its characters, that it might easily be mistaken for that ance. The *ethyl-ammonia* or *ethylia*, or *ethylamine*, has not only the fied odour of ammonia, but is powerfully alkaline, and combines ly with acids, forming salts, many of which may be crystallised. It might be expected, more inflammable than ammonia.

ne crystalline compound formed by the action of iodide of ethyle upon onia is the hydriodate of ethylamine—

$$C_4H_5I + N\begin{Bmatrix} H \\ H \\ H \end{Bmatrix} = N\begin{Bmatrix} C_4H_5 \\ H \\ H \end{Bmatrix} . HI$$

hydrogen expelled from the ammonia having taken the place of the le in the iodide, forming hydriodic acid, which remains in combina- with the ethylamine.

hloride of ethyle and bromide of ethyle, when heated with ammonia, l, respectively, the hydrochlorate and hydrobromate of ethylamine, but iodide of ethyle is preferred for this and similar experiments, as being *volatile, and, therefore,* more manageable in sealed tubes.

When the hydriodate of ethylamine is distilled with potash, it beh
just as hydriodate of ammonia would do if similarly treated—

$$NH_3.HI + KO = NH_3 + KI + HO$$

Hydriodate of ammonia. Ammonia.

$$NH_2.C_4H_5.HI + KO = NH_2.C_4H_5 + KI + HO.$$

Hydriodate of ethylamine. Ethylamine.

Ethylamine also combines with the oxygen-acids in the same ma
as ammonia—

Sulphate of ammonia, . . . $NH_3, HO.SO_3$
Sulphate of ethylamine, . . $NH_2.C_4H_5, HO.SO_3$

If any further proof were wanted that ethylamine is really composed ac
type of ammonia, it would be afforded by the circumstance, that ethylamine m
prepared by distilling cyanic ether with hydrate of potash.

Cyanic ether ($C_4H_5O.CyO = C_4H_5O.C_2NO$) is obtained by distilling eth
nate of potash with cyanate of potash—

$$KO.CyO + KO.C_4H_5O.2SO_3 = C_4H_5O.CyO + 2(KO.SO_3).$$

Cyanate of potash. Sulphovinate of potash. Cyanic ether.

Now, cyanic ether is simply cyanic acid, in which an equivalent of ethyle
the place of an equivalent of hydrogen—

Cyanic acid, . . . HO.CyO
Cyanic ether, . . . EO.CyO.

When cyanic acid is distilled with hydrate of potash, it yields amm
carbonate of potash—

$$HO.C_2NO + 2(KO.HO) = NH_3 + 2(KO.CO_2)$$

and since cyanic ether contains an atom of ethyle, in place of an atom of h
it would be expected to furnish an ammonia in which a similar displace
been effected—

$$EO.C_2NO + 2(KO.HO) = NH_2E + 2(KO.CO_2).$$

Cyanic ether. Ethylamine.

If ethylamine be again acted upon by an equivalent of iodide o
a second atom of hydrogen may be displaced by ethyle, and the hy
of *diethylamine* is obtained—

$$N\left\{\begin{matrix}C_4H_5\\H\\H\end{matrix}\right\} + C_4H_5I = N\left\{\begin{matrix}C_4H_5\\C_4H_5\\H\end{matrix}\right\}.HI$$

Ethylamine. Iodide of ethyle. Hydriodate of diethylamine.

and from this hydriodate the diethylamine is obtained by distilla
potash, as a colourless and inflammable liquid, strongly ammoni
having a much higher boiling point than ethylamine (134°·6 F.)
chemical relations diethylamine is a decided ammonia.

In order to remove the third atom of hydrogen, it is only nec
subject diethylamine to the action of iodide of ethyle—

$$N\left\{\begin{matrix}C_4H_5\\C_4H_5\\H\end{matrix}\right\} + C_4H_5I = N\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}.HI.$$

Diethylamine. Iodide of ethyle. Hydriodate of Triethylamine.

When this last hydriodate is distilled with potash, the triethyl
obtained as a colourless liquid, presenting the strongest eviden
relationship to ethylamine and diethylamine as well as to ammoni
powerfully alkaline, and boils at a higher temperature than diethy

* Just as ethylamine is obtained by the action of hydrate of potash upon cyani
ethylamine is formed when ethylate of potash (potassium-alcohol) acts upon cya

$$EO.C_2NO + 2(KO.EO) = NE_3 + 2(KO.CO_2).$$

e action of iodide of ethyle does not stop here, for if triethyla- again heated with it, an equivalent of that base combines with alent of the iodide to form the compound $N(C_4H_5)_3 . C_4H_5I$, which represented as hydriodate of triethylamine in which the place of rogen in the hydriodic acid is occupied by ethyle.

t will be remembered that the hydriodate of ammonia ($NH_3 . HI$) times regarded as the iodide of a hypothetical compound metal ium (NH_4), and it would appear admissible to view the above und as iodide of ammonium (NH_4I), in which the four atoms of gen are displaced by ethyle; it would then be called *iodide of tetre- monium* (NE_4I), or iodide of tetrethylium.

like the preceding compounds, the iodide of tetrethylium may be l with solution of potash without decomposition, but if a solution of substance be treated with oxide of silver, iodide of silver is formed, when the solution is filtered and evaporated *in vacuo* over sulphuric , it deposits needle-like crystals having the composition $N(C_4H_5)_4O . HO$. s substance, which is called the *hydrated oxide of tetrethylium*, is ctly similar in properties to the hydrates of potash and soda; it is liquescent, absorbs carbonic acid eagerly from the air, is exceedingly kaline and caustic, expels ammonia from its salts, forms soaps with the ts, and behaves in every respect like the hydrate of a fixed alkali. Its ste is very bitter as well as alkaline.

It is obviously not an ammonia, but is composed after the type of ydrate of potash ($KO . HO$), and contains, in place of the potassium, the rpothetical radical tetrethylium, $N(C_4H_5)_4$, or ammonium (NH_4) in which e four atoms of hydrogen have been displaced by ethyle.

The action of oxide of silver upon the iodide of tetrethylium is now telligible—

$$\underset{\text{Iodide of tetrethylium.}}{NE_4I} + AgO + HO = \underset{\text{Hydrated oxide of tetrethylium.}}{NE_4O . HO} + AgI.$$

The new alkali is easily decomposed; even at a temperature below the oiling point of water, it is resolved into triethylamine, olefiant gas, and ater—

$$N(C_4H_5)_4O . HO = \underset{\text{Triethylamine.}}{N(C_4H_5)_3} + C_4H_4 + 2HO.$$

It will be remembered that the solution of ammonia in water may be garded as containing the hydrated oxide of ammonium, for—

$$NH_3 + 2HO = NH_4O . HO$$

hich latter would be the true type of the hydrated oxide of tetrethylium; ut so great is the want of stability in this case, that all attempts to isolate he hydrated oxide of ammonium have resulted in the production of mmonia and water.

Like potash, the oxide of tetrethylium is capable of forming salts with he oxygen-acids without the intervention of an equivalent of water, thus—

Sulphate of potash, . . $KO . SO_3$
Sulphate of oxide of tetrethylium, $(NE_4)O . SO_3$.

It would naturally be expected that by the action of the iodides of other lcohol-radicals upon ammonia, compounds should be obtained correspond- *g to those belonging to the* ethyle series; thus we have—

(*Type*; ammonia NH_3).

Methylamine*	$NH_2.C_2H_3$	Diamylamine,	$NH(C$
Ethylamine,	$NH_2.C_4H_5$	Trimethylamine,	$N(C_2$
Amylamine,	$NH_2.C_{10}H_{11}$	Triethylamine,	$N(C_4$
Dimethylamine,	$NH.(C_2H_3)_2$	Triamylamine,†	$N(C_{10}$
Diethylamine,	$NH.(C_4H_5)_2$		

(*Type*; imaginary hydrated oxide of ammonium, $NH_4O.HO$

Hydrated oxides of—

Tetramethylium,	$N(C_2H_3)_4O.HO$
Tetrethylium,	$N(C_4H_5)_4O.HO$
Tetramylium,	$N(C_{10}H_{11})_4O.HO$

But even here, the elasticity of the types and the replacin the alcohol-radicals are not exhausted.

If methylamine ($NH_2.Me$) be acted upon by iodide of hydriodate of *methyl-ethylamine* is formed—

$$NH_2.Me + EI = NHMeE.HI$$

Methylamine. Iodide of ethyle. Hydriodate of methyl-ethyl

and by distilling this with potash, the methyl-ethylamine, mu the other ammonia bases, is obtained.

Again, on subjecting this base to the action of iodide o distilling the product with potash, a new ammonia base is which all three equivalents of hydrogen are replaced by diffe this base is called methyl-ethyl-amylamine, and its composi sented by the formula $N(C_2H_3)(C_4H_5)(C_{10}H_{11}) = NMeEAyl$

If we had started with aniline (phenylamine, $NH_2.C_{12}H_5$ experiment, treatment with iodide of methyle would ha methyl-aniline or methyl-phenylamine, $NH.C_{12}H_5.C_2H_3$; a this with iodide of ethyle, we should obtain ethyl-methyl $NC_{12}H_5.C_2H_3.C_4H_5$; the action of iodide of amyle u ammonia would give the iodide of methyl-ethyl-amylophen decomposing this with oxide of silver there would be hydrated oxide of methyl-ethyl-amylophenyl-ammonium—

$$N(C_2H_3)(C_4H_5)(C_{10}H_{11})(C_{12}H_5)O.HO$$

a base formed upon the hypothetical type of hydrated oxide in which each of the four equivalents of hydrogen is replace radical.

This complex substance affords an excellent example of between an empirical and a rational formula; its empi $C_{25}H_{29}NO_2$, which simply shows the result of its ultimate an nothing with respect to its constitution, which is at once c rational formula as above written is placed before us.

Phenylamine, $NH_2(C_{12}H_5)$, is found among the products of the tillation of rosaniline (p. 467), whilst ethyl-rosaniline (aniline-viol *phenylamine* or *ethyl-aniline*, $NH(C_{12}H_5)(C_4H_5)$, and phenyl-rosanili yields *di-phenylamine* or *phenyl-aniline*, $NH(C_{12}H_5)_2$.

* Methylamine, which is a gas at the ordinary temperature, is far more than any other gas; water dissolves 1150 volumes of methylamine, the resembling that of ammonia.

† Even the hypothetical hydrocarbon cetyle ($C_{32}H_{33}$), the radical of eth stituted for the nitrogen in ammonia. The base *tricetylamine*, $N(C_{32}H_{33})_3$ med, contains only 2 per cent. of nitrogen.

ylamine has also been obtained by digesting hydrochlorate of aniline with
e at a high temperature, when hydrochlorate of diphenylamine is obtained,
decomposed by a large excess of warm water, the diphenylamine rising to
e as an oil which solidifies on cooling. The change may be expressed by
ing equation :—

$$(C_{12}H_5).HCl + NH_2(C_{12}H_5) = NH(C_{12}H_5)_2.HCl + NH_3.$$

Hydrochlorate of aniline. Aniline. Hydrochlorate of diphenylamine.

lamine, $NH(C_{14}H_7)_2$, may be procured in a similar way by digesting hydro- f toluidine with toluidine.

-toluylamine, $NH(C_{12}H_5)(C_{14}H_7)$, is formed by the action of aniline on hydro- of toluidine, or by that of toluidine on hydrochlorate of aniline.

the action of nitric acid, di-phenylamine gives rise to di-nitro-diphenylamine, $H_4(NO_4)]_2$, in which the same type is preserved, though nitric peroxide (NO_4) tuted for one-fifth of the hydrogen in the phenyle.

treated with chloride of benzoyle ($C_{14}H_5O_2.Cl$), diphenylamine yields l-benzoylamine, $N(C_{12}H_5)_2(C_{14}H_5O_2)$.

ill be observed that certain of these bases derived from the alcohols ie same empirical formulæ as those derived from coal-tar and other , with which, however, they are by no means identical. Thus, tolui- $_{14}H_9N$) has the same composition as methyl-aniline ($NH.C_{12}H_5.C_2H_3$); former is a crystalline solid, and the latter an oily liquid. Again, oide of ethyle acts upon toluidine, an equivalent of hydrogen is ed by ethyle, and *ethylo-toluidine* is obtained. The *composition* base, $C_{14}H_6(C_4H_5)N$, is the same as that of methyl-ethyl-aniline, $_6)(C_4H_3)(C_{12}H_5)$, and as that of cumidine ($C_{18}H_{13}N$); but in their al properties these bodies exhibit such a difference as would be d from the difference in their *constitution*.

Investigation of the constitution of the alkaloids.—It will be evi- at the principles developed in the experiments just described may lied in investigating the constitution of the bases extracted from

Let it be supposed that ethylamine (C_4H_7N) was a vegetable f unknown constitution; when it was found that by the action of f ethyle two out of the seven atoms of hydrogen could be displaced, d be at once inferred that these two atoms occupied a very different a from the other five, and that the constitution of the compound be more properly expressed by writing the formula $C_4H_5.H_2N$. lying the same principle to the examination of the natural alkaloid, ($C_{16}H_{15}N$), it was found possible, by the action of iodide of methyle, ve only one atom of the hydrogen, so that the formula $C_{16}H_{14}.H.N$ more correctly represent the constitution of coniine, which might be garded as ammonia in which two atoms of the hydrogen have been ed by the group $C_{16}H_{14}$, or in which each of these atoms has been ed by the group C_8H_7.

e were acquainted with an iodide of this group, we have every to expect that its action upon ammonia would lead us to the l formation of coniine.*

tine, morphine, and codeine will not part with any of their hydro- der the action of iodide of ethyle, and must therefore be placed ie same footing as triethylamine, $N(C_4H_5)_3$, in which all three atoms

group C_8H_7 is often assumed as the radical of butyric acid ($C_8H_8O_4$), and it is a rious coincidence, that when acted upon by nitric acid, coniine actually y id.

of hydrogen are already replaced. Upon this view they would be represented thus—

Nicotine, $N(C_{10}H_7)'''$
Morphine, $N(C_{34}H_{19}O_6)'''$
Codeine, $N(C_{36}H_{21}O_6)'''$

The mark (''') signifying that the groups are *triatomic*, or have the replacing value as three atoms of hydrogen. When these bases are acted upon by the iodides of alcohol-radicals, there are formed, as would be expected, iodides upon the type NH_3I, from which may be obtained alkalies resembling the hydrated oxide of tetrethylium. Thus we have the hydrated oxides of

Methyl-morphyl-ammonium, $N(C_{34}H_{19}O_6)'''(C_2H_3)O.HO$
Ethyl-codeyl-ammonium, $N(C_{36}H_{21}O_6)'''(C_4H_5)O.HO$
Ethyl-nicotyl-ammonium, $N(C_{10}H_7)'''(C_4H_5)O.HO$

397. *Poly-ammonias.*—In speculating upon the constitution of vegetable bases, it must not be forgotten that some of them contain equivalents of nitrogen; this is the case, for example, with cinchonine ($C_{40}H_{24}N_2O_2$), quinine ($C_{40}H_{24}N_2O_4$), and strychnine ($C_{42}H_{22}N_2O_4$). If the whole of the nitrogen in these bases be due to the ammonia type, they must be composed after the type of a double atom of ammonia, N_2H_6. In the case of strychnine, it is found that the action of iodide of ethyle fails to remove any portion of the hydrogen, so that if the base be really composed after the ammonia type, it must be represented by two atoms of ammonia (N_2H_6), in which the whole of the hydrogen has been displaced by the group ($C_{42}H_{22}O_4$), when its formula would be $N_2(C_{42}H_{22}O_4)''''$, the replacing group in this case being *hexatomic*, or equivalent to six atoms of hydrogen. That it is by no means necessary for each atom of hydrogen to be displaced by a single group or radical, is seen in a great many organic compounds; thus, in chloroform $(C_2H)Cl_3$, we have the triatomic group C_2H (commonly called formyle) occupying the position of three atoms of hydrogen which would be required to combine with the three atoms of chlorine; again, in Dutch liquid, $(C_4H_4)Cl_2$, we have the diatomic group C_4H_4 (ethylene) occupying the place of two atoms of hydrogen.

If the view above explained with respect to the constitution of some of the natural alkaloids be correct, it ought to be possible to form artificially a base in which two or three atoms of hydrogen had been displaced by means of a diatomic or triatomic radical.

398. *Diamines.*—When olefiant gas or ethylene, C_4H_4, is brought in contact with bromine, the compound $C_4H_4Br_2$, corresponding to Dutch liquid ($C_4H_4Cl_2$), is obtained, and from the action of ammonia upon this *bibromide of ethylene*, there is derived a new alkaline base, having the composition $N_2H_4(C_4H_4)''$, or two atoms of ammonia (N_2H_6), in which the diatomic ethylene replaces two atoms of hydrogen. Such bases, formed upon the double ammonia type, are called *diamines*, whilst those which correspond to a single atom of ammonia are called *monamines*. The base above mentioned is named *ethylene-diamine*. The diamines, like the double atom of ammonia from which they are derived, are capable of combining with two equivalents of hydrochloric or any similar acid, which is implied by stating that they are *diacid*.

When Dutch liquid (*bichloride of ethylene*, $(C_4H_4)''Cl_2$) is heated to 300° F. with strong ammonia in a sealed tube, an action takes place corresponding to that of

atom of hydrochloric acid (H_2Cl_2) upon a double atom of ammonia (N_2H_6), would give rise to a double atom of hydrochlorate of ammonia ($N_2H_6.H_2Cl_2$); product of the action of Dutch liquid upon ammonia ($N_2H_4(C_4H_4)_2''Cl_2$), the of four atoms of hydrogen are occupied by two atoms of the diatomic group). But here the correspondence ceases, for whilst the hydrochlorate of nia, when decomposed with oxide of silver, would yield ammonia and chloride er, the new compound, when thus treated, yields a fixed alkaline base, resem- hydrate of potash, and having the composition $N_2H_4(C_4H_4)_2''O_2.2HO$, which ents a double atom of the hypothetical hydrated oxide of ammonium $_4O.HO$), in which four atoms of hydrogen have been displaced by two atoms diatomic ethylene. The name *hydrated oxide of diethylene-diammonium* ex- the composition of this substance, which is remarkable for its stability, a rature above 300° F. being required to effect its decomposition, when it hes a volatile alkali, having the composition $N_2H_2(C_4H_4)_2''$, and called di- ne-diamine, being evidently formed from a double atom of ammonia, in which toms of hydrogen are replaced by two atoms of the diatomic ethylene. Its tion may be explained by the equation—

$$N_2H_4(C_4H_4)_2''O_2.2HO = N_2H_2(C_4H_4)_2'' + 4HO.$$

ing upon the new ammonia with iodide of ethyle (C_4H_5I), the two equiva- f hydrogen may be displaced by ethyle, yielding *diethyl-diethylene-diamine*, $H_5)_2(C_4H_4)_2''$, or a double atom of ammonia (N_2H_6), in which H_2 are replaced atoms of ethyle, and H_4 by two atoms of ethylene.

treating phenylamine (aniline), $NH_2(C_{12}H_5)$, with bichloride of ethylene liquid), the *diphenyl-diethylene-diamine*, $N_2(C_{12}H_5)_2(C_4H_4)_2''$, is obtained, represents a double atom of ammonia (N_2H_6), in which H_2 are replaced by oms of phenyle, and H_4 by two atoms of ethylene. By the action of chloro- pon aniline, *formyl-diphenyl-diamine*, $N_2(C_2H)'''(C_{12}H_5)_2H$, has been obtained, ch H_3 are replaced by the triatomic formyle (C_2H), and H_2 by phenyle.

as been seen that phenylamine is produced by the deoxidising action of ferrous e upon nitrobenzole ($C_{12}H_5.NO_4$). When di-nitrobenzole is treated in a r way, *phenylene-diamine*, $N_2H_4(C_{12}H_4)''$ is obtained, which is evidently derived a double atom of ammonia, in which H_2 are replaced by the diatomic group *ene* ($C_{12}H_4$), which bears the same relation to phenyle ($C_{12}H_5$) as ethylene) bears to ethyle (C_4H_5). By treating di-nitrotoluole and di-nitrocumole with s acetate, *tolylene-diamine* and *cumylene-diamine* are obtained, which are di- nias, in which H_2 are replaced by the diatomic radicals *tolylene* ($C_{14}H_6)''$ and *ne* ($C_{18}H_{10})''$. These three diamines are called the *aromatic diamines*, since the nic groups phenylene, tolylene, and cumylene are closely connected, through le ($C_{12}H_6$), toluole ($C_{14}H_8$), and cumole ($C_{18}H_{12}$), with the *aromatic acids*, benzoic $_6O_4$), toluic ($C_{16}H_8O_4$), and cuminic ($C_{20}H_{12}O_4$).

aniline ($C_{24}H_{14}N_2$) is obtained as a secondary product in the manufacture of e, with which it is polymeric. Its properties are very different from those of e, for it is solid at the ordinary temperature, forming silky needles which melt heated, and boil beyond the range of the thermometer, distilling unchanged. ibines with acids, forming beautiful crystalline salts, the study of which proves e a diamine.

9. *Triamines.*—The triamines are formed upon the type of a treble of ammonia (N_3H_9), in which the hydrogen is replaced either entirely part by other radicals. Thus, *diethylene-triamine*, $N_3H_5(C_4H_4)_2''$, *riethylene-triamine*, $N_3H_3(C_4H_4)_2''$, are obtained by the action of bi- ide of ethylene ($C_4H_4Br_2$) upon ammonia. They are powerfully ine liquids, which are capable of absorbing carbonic acid from the The triamines are generally capable of forming three classes of salts, *nonacid*, *diacid*, and *triacid* salts, containing respectively one, two, hree equivalents of acid.

ethylene-di-ethyl-triamine, $N_3H_3(C_4H_4)_2''(C_4H_5)_2$, is produced by the joint of ethylamine and ammonia upon bibromide of ethylene—

$$2[(C_4H_4)''Br_2] + 3NH_2(C_4H_5) + NH_3 = N_3H_3(C_4H_4)_2''(C_4H_5)_2.3HBr + NH_2(C_4H_5).HBr.$$

It forms splendidly crystallised salts, and is evidently derived from the ammonia (N_3H_9), by the substitution of two atoms of ethylene (C_4H_4) and two atoms of ethyle (C_4H_5)$_2$ for H_3.

Carbotriamine (guanidine), $N_3H_5C^{iv}$, is a treble atom of ammonia, in atoms of hydrogen are replaced by one atom of tetratomic carbon (see p. is formed by heating ammonia with subcarbonate (orthocarbonate) of sealed tube to about 300° F.

$$2(2C_4H_5O.CO_2) + 3NH_3 + 2HO = N_3H_5C_2''.2HO + 4(C_4$$

The change is more clearly explained by representing the subcarbonate formed upon the type of four equivalents of water (H_4O_4) in which H_2 by $(C_4H_5)_2$, and the remaining H_2 by C″ (as in $C''O_2$).

$$2\left[\begin{matrix}(C_4H_5)_2\\ C''\end{matrix}\middle|O_4\right] + 3NH_3 + 2HO = N_3H_5C_2''.2HO +$$

Subcarbonate of ethyle. Guanidine.

Guanidine may also be obtained by heating chloropicrine in a sealed an alcoholic solution of ammonia, to 212° F., when the following reacti

$$C_2Cl_3(NO_4) + 3NH_3 = N_3H_5C_2''.HCl + 2HCl + NO_2$$

Chloropicrine. Hydrochlorate of guanidine.

It will be remembered that the subcarbonate of ethyle itself is ob action of sodium upon an alcoholic solution of chloropicrine (p. 528).

Melaniline, $C_{26}H_{13}N_3$, a crystalline base, produced by the action o cyanogen upon aniline, may be regarded as *diphenyl-guanidine*, N_3H or guanidine in which two atoms of phenyle have replaced two of hyd

The beautiful aniline dyes appear to be salts of certain triamines replacement of the hydrogen in a treble atom of ammonia by hydroca

According to Hofmann, rosaniline, the base of the aniline red pr action of oxidising agents upon aniline containing toluidine, is poss *ditolylene-triamine*, $N_3(C_{12}H_4)''(C_{14}H_6)_2''H_3.2HO$, the phenylene being the aniline, $NH_2(C_{12}H_5)$, and the tolylene from the toluidine, $NH_2(C$ line blue, formed by the action of aniline upon aniline red, would *ditolylene-triphenyl-triamine*, $N_3(C_{12}H_4)''(C_{14}H_6)_2''(C_{12}H_5)_3.2HO$, havin from rosaniline by the substitution of three atoms of phenyle for violet, the result of the action of iodide of ethyle upon rosaniline, woul *ditolylene-triethyl-triamine*, $N_3(C_{12}H_4)''(C_{14}H_6)_2''(C_4H_5)_3.2HO$, or rosa ing three atoms of ethyle in place of H_3.

The *trichloride of diethylene-triammonium*, $N_3(C_4H_4)_2''H_3.Cl_3$, has tained.

400. *Tetramines* are formed upon the type of four atoms and therefore contain four atoms of nitrogen, and are able to four atoms of a hydrogen acid. Thus, if bibromide of ethyle to act upon ethylene-diamine in the presence of hydrobro hydrobromate of triethylene-tetramine is obtained—

$$(C_4H_4)''Br_2 + 2N_2(C_4H_4)''H_4 + 2HBr = N_4(C_4H_4)_2''H$$

Bibromide of ethylene. Ethylene-diamine. Hydrobrom triethylene-t

and if this be decomposed with oxide of silver, a strongly tion is obtained, which contains triethylene-tetramine, $N_4(C$ a quadruple atom of ammonia (N_4H_{12}), in which half the replaced by three atoms of diatomic ethylene.

By acting on $C_4H_4Br_2$ with ethylamine, a salt is obtained, havi sition $N_4(C_4H_4)_5''(C_4H_5)_4H_2.Br_4$, representing four atoms of bromide ($N_4H_{12}Br_4$) in which H_{10} are replaced by $5(C_4H_4)''$, and H_4 by $(C_4H_5$ bromide a strongly alkaline base, the hydrated oxide of *pentethyle ammonium*, $N_4(C_4H_4)_5''(C_4H_5)_4H_2O_4.4HO$, is obtained, which is formed of four atoms of the imaginary hydrated oxide of ammonium (NH_4O

ction of iodide of ethyle (C_4H_5I) upon this base replaces each of the remaining atoms of hydrogen by ethyle, yielding $N_4(C_4H_4)_6''(C_4H_5)_5HO_4 . 4HO$ and $N_4(C_4H_4)_6''(C_4H_5)_6O_4 . 4HO$.

a diethylamine ($NH(C_4H_5)_2$) acts on bibromide of ethylene, the bromide of *ene-octethyl-tetrammonium*, $N_4(C_4H_4)_2''(C_4H_5)_8H_2 . Br_4$, is obtained, which also es a powerfully alkaline base, $N_4(C_4H_4)_2''(C_4H_5)_8H_2O_4 . 4HO$.

. We are not entirely dependent upon purely artificial processes e ammonia bases containing alcohol-radicals. Many processes of faction furnish certain of these bases which had hitherto been overd in consequence of their resemblance to ammonia. Thus, putrefour yields ethylamine, trimethylamine, and amylamine; trimethyne is also found in the roe of herrings, as also in putrefied urine and e *chenopodium vulvaria;* it may also be obtained by distilling ergot e with potash. Methylamine, ethylamine, *propylamine* ($NH_2 . C_6H_7$), *Tamine* ($NH_2 . C_5H_9$), or *petinine*, and amylamine, are found among products of the destructive distillation of bones.

402. *Ammonias and ammonium bases containing phosphorus, arsenic, d antimony.*—It might be expected that the ammonia type was not sceptible of any further modifications, but it has been found that even e nitrogen of that type may be represented by other elements which are emically related to it.

Antimony, arsenic, and phosphorus, it will be remembered, all form ompounds with three atoms of hydrogen, SbH_3, AsH_3, and PH_3, which ay be regarded as formed upon the ammonia type. Neither of these ubstances, however, possesses any alkaline character, the last alone being apable of combining with certain acids (hydrobromic and hydriodic).

Mention has already been made of the circumstance that compounds corresponding to antimonietted, arsenietted, and phosphuretted hydrogen may be obtained, in which the place of the hydrogen is occupied by certain alcohol-radicals; but in these cases the hydrogen does not admit of partial replacement, only those compounds which correspond to triethylamine and trimethylamine having been obtained.

Triethylstibine, $Sb(C_4H_5)_3$, and *triethylarsine*, $As(C_4H_5)_3$, have already been noticed amongst another class of bodies to which they seem properly to belong, since they are not capable of forming salts corresponding to those of ammonia, and appear really to be composed after the types SbO_3 and AsO_3 (*see* p. 536).

With *triethylphosphine*, however, the case is different; this substance, $P(C_4H_5)_3$, is a true ammonia, capable of forming salts with the acids, like ethylamine, although exhibiting, unlike that body, a very powerful tendency to combine directly with two equivalents of oxygen and sulphur, to form compounds resembling those of the arsenic and antimony series (*see* p. 537), and formed upon the type of phosphoric acid (PO_5). Thus we have—

Binoxide of triethylphosphine,	PE_3O_2
Bisulphide, ...	PE_3S_2

and the corresponding compounds containing methyle.

Triethylphosphine is obtained by the action of terchloride of phosphorus upon zinc-ethyle, $PCl_3 + 3ZnE = PE_3 + 3ZnCl$. It is a volatile liquid of a very peculiar powerful odour, the vapour of which, when mixed with oxygen, explodes with great violence at a temperature far *below 212°*.

oxide of tetrethylium, being powerfully caustic and resemblance to hydrate of potash.

A very remarkable base has also been obtained, type of a double atom of the imaginary hydrated ($N_2H_5O_2 . 2HO$), in which one atom of nitrogen h phosphorus, and the other by arsenic, whilst of the are replaced by the diatomic radical ethylene (C_4H_4 by ethyle. This base has been styled the hydrate hexethyle-diphospharsonium, and its formula is—

$$PAs\,(C_4H_4)''(C_4H_5)_6O_2 . 2HO .$$

This base combines with two equivalents of acid behaves in every respect as a double equivalent would do.

By acting upon triethylphosphine with *chlorofo* ing the triatomic radical formyle $(C_2H)'''$, a chlori which is composed upon the type of three atoms monium ($3NH_4Cl = N_3H_{12}Cl_3$), in which one-fou is replaced by formyle and the rest by ethyle; the chloride is therefore $(P_3(C_2H)'''(C_4H_5)_9Cl_3)$; from th salts have been obtained containing the correspond with three equivalents of the acids, but the hydrate been obtained.

$$3P(C_4H_5)_3 + (C_2H)'''Cl_3 = P_3(C_2H)'$$

Triethylphosphine. Chloroform. Trichloride triph

403. The insight into the constitution of the bases derive has been acquired in the researches detailed above, has ind vour to apply the same principles to certain inorganic base by the action of metallic salts.

Thus, by the action of (proto) chloride of platinum upo a compound is obtained which may be regarded as simply this is treated with oxide of silver, the Cl is removed in silver, and a caustic alkaline base is separated, which has the

Chloride of *plato-triethyl-phosphonium*, . .	$PPt(C_4H_5)_3 . Cl$
" " *arsonium*, . .	$AsPt(C_4H_5)_3 . Cl$
" " *stibonium*, . .	$SbPt(C_4H_5)_3 . Cl$

sponding salts have also been obtained containing gold in the place of , and forming beautiful *colourless* crystals.

ome bases, chlorine, bromine, and even nitric peroxide (NO_4) have troduced in the place of hydrogen into the alcohol-radical, but in se cases the basic energy is diminished by such substitution, and in ltogether destroyed.
s, in the aniline (phenylamine) series, we have—

Chloraniline, . . .	$NH_2(C_{12}H_4Cl)$, weak base.
Dichloraniline, . . .	$NH_2(C_{12}H_3Cl_2)$, weaker base.
Trichloraniline, . . .	$NH_2(C_{12}H_2Cl_3)$, neutral.
Nitraniline, . . .	$NH_2[C_{12}H_4(NO_4)]$, weak base.
Dinitraniline, . . .	$NH_2[C_{12}H_3(NO_4)_2]$, neutral.

4. *Amides.*—When oxalate of ammonia ($NH_4O . C_2O_3$) is subjected stillation, a white, crystalline sparingly soluble substance is obtained, n has been named *oxamide*, and is represented by the formula $. C_2O_2$. This substance is derived from the ammonia-salt by the loss equivalents of water—

$$NH_4O . C_2O_3 - 2HO = NH_2 . C_2O_2$$

its close relationship to oxalate of ammonia is shown by the circum- ce that it is reconverted into that salt, if heated with water in a d tube to 436° F., or by simply boiling it with water to which a acid or alkali has been added.
xamide is more readily prepared by decomposing oxalic ether with ionia, when it is obtained as a white crystalline precipitate—

$$\underset{\text{Oxalic ether.}}{C_4H_5O . C_2O_3} + NH_3 = \underset{\text{Alcohol.}}{C_4H_5O . HO} + \underset{\text{Oxamide.}}{NH_2 . C_2O_2} .$$

one of the compound ammonias, such as ethylamine and aniline, be loyed instead of ammonia, *ethlyoxamide* and *oxanilide* are produced—

$$\underset{\text{Oxalic ether.}}{H_5O . C_2O_3} + \underset{\text{Ethylamine.}}{NH_2 . C_4H_5} = C_4H_5O . HO + \underset{\text{Ethyloxamide.}}{NH . C_4H_5 . C_2O_2} ,$$

$$H_5O . C_2O_3 + \underset{\text{Aniline.}}{NH_2 . C_{12}H_5} = C_4H_5O . HO + \underset{\text{Oxanilide.}}{NH . C_{12}H_5 . C_2O_2} .$$

xamide is the representative of a large class of bodies, known as the *les*, which may be defined as substances capable of being converted, by assimilation of the elements of two equivalents of water, into the ionia-salts from which they are derived.
ome other interesting members of this class are here enumerated, ther with the corresponding ammonia-salts—

ormamide, . . . $NH_2 . C_2HO_2$	Formiate of ammonia, $NH_4O . C_2HO_3$
cetamide, . . . $NH_2 . C_4H_3O_2$	Acetate, ... $NH_4O . C_4H_3O_3$
utyramide, . . . $NH_2 . C_8H_7O_2$	Butyrate, ... $NH_4O . C_8H_7O_3$
enzamide, . . . $NH_2 . C_{14}H_5O_2$	Benzoate, ... $NH_4O . C_{14}H_5O_3$

s evident that these amides may be regarded as derived from ammonia he substitution of a compound group for one of the three atoms of ogen.

When binoxalate of ammonia ($NH_4O.C_2O_3$, $HO.C_2O_3$) is distilled at a moderate heat, a solid acid substance is left in the retort, which is known as *oxamic acid*, $NH_2.C_2O_2$, $HO.C_2O_3$, and may be regarded as compounded of oxamide (derived from neutral oxalate of ammonia), with the extra equivalent of hydrated oxalic acid. That it contains no oxalic acid as such is proved by its yielding soluble crystallisable salts with lime and baryta, both which yield insoluble salts with oxalic acid.

When the solution of oxamic acid in water is boiled, it is reconverted into the binoxalate of ammonia—

$$\underset{\text{Oxamic acid.}}{NH_2.C_2O_2, HO.C_2O_3} + 2HO = \underset{\text{Binoxalate of ammonia.}}{NH_4O.C_2O_3, HO.C_2O_3}.$$

Oxamic acid is the representative of a limited class of acids formed in a similar manner.*

405. *Nitriles.*—When oxalate of ammonia is mixed with anhydrous phosphoric acid and distilled, it loses four equivalents of water, leaving cyanogen, $NH_4O.C_2O_3 - 4HO = C_2N$.

In a similar manner, benzoate of ammonia yields *benzonitrile*—

$$\underset{\text{Benzoate of ammonia.}}{NH_4O.C_{14}H_5O_3} - 4HO = \underset{\text{Benzonitrile.}}{C_{14}H_5N}.$$

The new compound is an oil which has a powerful odour of bitter almonds, and is reconverted into benzoate of ammonia by boiling with dilute acids or alkalies.

The term *nitrile* is applied to all similar substances which are derived from ammoniacal salts by the loss of four equivalents of water, and are capable of reconversion into those salts. It will be remembered that many of these nitriles are identical with the cyanides of the alcohol radicals.

Oxalonitrile,	NC_2	=	Cy, cyanogen.
Formonitrile,	NC_2H	=	HCy, hydrocyanic acid.
Acetonitrile,	NC_4H_3	=	$C_2H_3.C_2N$, cyanide of methyle.
Propionitrile,	NC_6H_5	=	$C_4H_5.C_2N$, ,, ethyle.
Benzonitrile,	$NC_{14}H_5$	=	$C_{12}H_5.C_2N$, ,, phenyle.

A by no means numerous class of substances, frequently spoken of the *imides*,† are obtained by the action of heat upon the acid ammonia salts of certain bibasic acids, by the loss of four equivalents of water, thus

$$\underset{\text{Bicamphorate of ammonia.}}{NH_4O.HO.C_{20}H_{14}O_6} - 4HO = \underset{\text{Camphorimide.}}{NH.C_{20}H_{14}O_4}.$$

406. If the amides be regarded as immediately derived from ammonia by substitution, their want of alkaline properties must be ascribed to the introduction of electro-negative radical in place of the hydrogen (*see* p. 520).

Thus, if oxalic acid be regarded as $HO.(C_2O_2)O$, the hydrated oxide of ox, then oxamide may be viewed as ammonia, in which one atom of hydrogen has displaced by that radical; $N\left\{\begin{matrix}(C_2O_2)\\H_2\end{matrix}\right.$

* Strictly speaking, oxalic acid being a bibasic acid, $2HO.C_4O_6$, its ammoni should be written $2NH_4O.C_4O_6$, when oxamide would become $N_2H_4.C_4O_6$, and the for of oxamic acid would be doubled, but this would in no way affect the general prin stated in the text.

† This designation was originally employed upon the supposition that these bodies 'n the imaginary radical imidogen, NH; and, in a similar manner, the amides pposed to contain amidogen, NH_2.

n, if benzoic acid and salicylic acid, respectively, be regarded as hydrated of benzoyl, $(C_{14}H_5O_2)O.HO$, and of salicyle, $(C_{14}H_5O_4)O.HO$, then their amides be represented as—

$$\text{Benzamide, } N\left\{\begin{matrix}C_{14}H_5O_2\\H\\H\end{matrix}\right.$$

$$\text{Salicylamide, } N\left\{\begin{matrix}C_{14}H_5O_4\\H\\H\end{matrix}\right.$$

should be possible to procure them from ammonia by processes similar to hich furnishes ethylamine, &c. It is found that when chloride of benzoyle is l with ammonia, benzamide is really produced—

$$\underset{\text{Chloride of benzoyle.}}{C_{14}H_5O_2.Cl} + 2NH_3 = \underset{\text{Benzamide.}}{NH_2.C_{14}H_5O_2} + NH_4Cl.$$

we ought also to be able to carry the substitution farther by displacing the ining hydrogen; accordingly, when benzamide and salicylamide are heated er, ammonia is disengaged, and benzoyl-salicylamide obtained—

$$N\left\{\begin{matrix}C_{14}H_5O_2\\H\\H\end{matrix}\right. + \left\{\begin{matrix}C_{14}H_5O_4\\H\\H\end{matrix}\right. = N\left\{\begin{matrix}C_{14}H_5O_2\\C_{14}H_5O_4\\H\end{matrix}\right. + NH_3.$$

Benzamide. Salicylamide. Benzoyl-salicylamide.

ides have even been obtained in which the three atoms of hydrogen in nia are displaced by different radicals.

evident that the imides might be regarded as ammonias in which two atoms rogen have been replaced by a diatomic radical, thus—

$$\text{Camphorimide, } N\left\{\begin{matrix}(C_{20}H_{14}O_2)''\\H\end{matrix}\right.$$

e nitriles, as ammonias in which all the hydrogen has been replaced by a nic radical, but experimental evidence is scarcely in favour of these views.

he amides be really derivatives from ammonia, it would be expected that r bodies should be derived from phosphuretted hydrogen (PH_3). An example e is furnished by *tribenzoyl-phosphide*, $P(C_{14}H_5O_2)_3$, which is obtained by the of chloride of benzoyle upon phosphuretted hydrogen.

$$\underset{\text{Chloride of benzoyle.}}{PH_3 + 3(C_{14}H_5O_2.Cl)} = \underset{\text{Tribenzoyl-phosphide.}}{P(C_{14}H_5O_2)_3} + 3HCl.$$

7. *Metal-amides.*—The possibility of substituting metals for the gen in ammonia has only recently been fully established, though it had been known that when potassium and sodium were heated in gaseous nia, hydrogen was evolved, and *potassamide* and *sodamide* were ced—

$$NH_3 + K = NH_2K + H.$$

potassamide is heated, ammonia is evolved, and *tripotassamide*) produced—

$$3(NH_2K) = NK_3 + 2NH_3.$$

ammoniacal gas be passed into an ethereal solution of zinc-ethyle, de of ethyle is evolved, and a white amorphous precipitate of *nide* separates—

$$\underset{\text{Zinc-ethyle.}}{NH_3 + C_4H_5.Zn} = \underset{\text{Zincamide.}}{NH_2.Zn} + \underset{\text{Hydride of ethyle.}}{C_4H_5.H}.$$

zincamide is brought in contact with water, it is decomposed with tion of heat, yielding hydrated oxide of zinc and ammonia—

$$NH_2Zn + 2HO = NH_3 + ZnO.HO.$$

decomposing action of zinc-ethyle upon the bases derived

ammonia is parallel with that upon ammonia itself. The aniline—

$$\underset{\text{Aniline.}}{NH_2.C_{12}H_5} + \underset{\text{Zinc-ethyle.}}{C_4H_5Zn} = \underset{\text{Zinc-phenylimide.}}{NH.Zn.C_{12}H_5} + \underset{\text{Hydride of e}}{C_4H_5.H}$$

When the zinc-phenylimide is treated with water, of course ani produced.

When diethylamine is heated with zinc-ethyle—

$$\underset{\text{Diethylamine.}}{N(C_4H_5)_2H} + C_4H_5Zn = \underset{\text{Diethylzincamine.}}{N(C_4H_5)_2Zn} + C_4H_5.H.$$

When zincamide is heated above 400° F., it is decomposed in nia and *nitride of zinc* (NZn_3), which represents ammonia, in three atoms of hydrogen are replaced by zinc—

$$\underset{\text{Zincamide.}}{3(NH_2Zn)} = \underset{\text{Nitride of zinc.}}{NZn_3} + 2NH_3.$$

The nitride of zinc is a grey powder, which is unaffected by a r air be excluded. If it be moistened with water, it become being decomposed with great violence, according to the equatio

$$NZn_3 + 6HO = NH_3 + 3(ZnO.HO).$$

It might be anticipated that if the amides be truly formed ammonia-type, they should behave towards zinc-ethyle in the sa as ammonia and aniline.

By heating oxamide with zinc-ethyle, one of its atoms of hyd be replaced by zinc—

$$\underset{\text{Oxamide.}}{NH_2.C_2O_2} + ZnC_4H_5 = \underset{\text{Zinc-oximide.}}{NH.Zn.C_2O_2} + C_4H_5.H$$

In a similar manner, acetamide ($NH_2.C_4H_3O_2$) is converted acetimide ($NHZn.C_4H_3O_2$). These bodies are reconverted int responding amides and oxide of zinc, when treated with water

Derivatives of the Alcohols.

408. *Chloroform.*—Among the useful substances prepared fr of the alcohol series, *chloroform* (C_2HCl_3) occupies a promine

It is prepared by distilling 1 part of alcohol with 6 parts of lime, and 24 parts of water, until about 1½ part has p the distilled liquid, consisting chiefly of water and chlorofor into two layers, the heavier being chloroform (sp. gr. 1·5). aqueous layer having been drawn off by a siphon, the c shaken with oil of vitriol to remove certain volatile oils, whi tilled over with it, and as soon as it has risen to the surface vitriol, it is drawn off and rectified by distillation, until it bo at 142° F.

The chemical change involved in the preparation of chloro to consist of two distinct stages, in the first of which the al verted into *chloral* by the action of the chlorine furnished by of lime, $\underset{\text{Alcohol.}}{C_4H_6O_2} + Cl_8 = \underset{\text{Chloral.}}{C_4HCl_3O_2} + 5HCl$; the hydrochlo course, neutralised by the lime. In the second stage, the chl upon by the hydrate of lime, which is always present in chloride of lime, and is converted into chloroform and form

$$\underset{\text{Chloral.}}{C_4HCl_3O_2} + CaO.HO = \underset{\text{Formiate of lime.}}{CaO.C_2HO_3} + \underset{\text{Chloroform.}}{C_2HCl_3}.$$

Chloroform is remarkable for its very fragrant odour, and for the power of its vapour to produce insensibility to pain, for which purpose it is largely used in surgical operations. This property is not peculiar to chloroform, but is possessed in different degrees by most other liquids of powerful ethereal odour, such as ordinary ether, bisulphide of carbon, bichloride (or perchloride) of carbon, &c. Chloroform is also used for dissolving caoutchouc, which it takes up more readily and abundantly than any other liquid, and is employed for extracting the poisonous alkaloids (particularly strychnine), when mixed with organic matters. The name chloroform has been conferred upon this substance on the supposition that it contained the radical of formic acid (formyle C_2H), and it is sometimes called the *terchloride of formyle*. This belief is encouraged by its behaviour with an alcoholic solution of potash, when it yields formiate of potash and chloride of potassium—

$$\underset{\text{Chloroform.}}{C_2HCl_3} + 4(KO.HO) = \underset{\text{Formiate of potash.}}{KO.C_2HO_3} + 3KCl + 4HO.$$

But the processes by which it may be formed would lead us to regard it as a substitution-product from marsh-gas (hydride of methyle, $C_2H_3.H$). If marsh-gas be diluted with an equal volume of carbonic acid, and to 1 volume of this mixture at least $1\frac{1}{2}$ volume of chlorine be added, chloroform is slowly produced, $C_2H_4 + Cl_6 = 3HCl + C_2HCl_3$. Chloroform is also formed by the action of chlorine upon chloride of methyle—

$$C_2H_3Cl + Cl_4 = C_2HCl_3 + 2HCl.$$

Wood-spirit (hydrated oxide of methyle) may be employed instead of alcohol for the preparation of chloroform.

If chloroform be distilled in a current of chlorine, it is converted into bichloride of carbon, $C_2HCl_3 + Cl_3 = C_2Cl_4 + HCl$. When chloroform is heated with amalgam of potassium, acetylene (C_4H_2) is disengaged, which is polymeric with the hypothetical radical formyle C_2H.

Bromoform (C_2HBr_3) and *Iodoform* (C_2HI_3) have no practical interest.

Chloral ($C_4HCl_3O_2$), which has been mentioned as resulting from the action of chlorine upon alcohol, may be regarded as aldehyde ($C_4H_4O_2$), in which 3 atoms of hydrogen are replaced by chlorine.

The most interesting feature of chloral, which is a colourless oily liquid, is its spontaneous transformation into a porcelain-like mass, which has the same composition as the liquid, and may be reconverted into it by distillation.

409. *Perfume-ethers.*—Certain of the compound ethers, formed by the combination of oxide of ethyle and its analogues with the acids of the acetic series, are employed in perfumery and confectionery.

Thus, the *butyrate of ethyle*, or *butyric ether* ($C_4H_5O.C_8H_7O_3$), prepared by distilling butyrate of potash with alcohol and sulphuric acid, has a decided flavour of pine apples. *Acetate of amyle* ($C_{10}H_{11}O.C_4H_3O_3$) has a very strong resemblance in taste and smell to the jargonelle pear; it is obtained by distilling fousel oil (hydrated oxide of amyle) with acetate of soda and sulphuric acid.

The *valerianate of amyle*, which has the flavour of apples, and is known as *apple-oil*, is obtained by distilling fousel oil with sulphuric acid and bichromate of potash, when the chromic acid of the latter oxidises one

portion of the hydrated oxide of amyle ($C_{10}H_{11}O.HO$), converting it into valerianic acid ($C_{10}H_9O_3.HO$), which then unites with another portion of oxide of amyle, forming the valerianate of amyle ($C_{10}H_{11}O.C_{10}H_9O_3$).

410. ALDEHYDES—*Vinic or acetic aldehyde.*—It has been already noticed (p. 492) that a considerable loss of alcohol has occasionally taken place in the manufacture of vinegar, in consequence of the formation of aldehyde ($C_4H_4O_2$) instead of acetic acid ($C_4H_4O_4$) by a partial oxidation of the alcohol. In order to prepare aldehyde in quantity, alcohol is distilled with sulphuric acid and binoxide of manganese, or with sulphuric acid and bichromate of potash, or it may be oxidised by chlorine in the presence of water.

Three parts of binoxide of manganese in fine powder are introduced into a retort, and a mixture of 3 parts of sulphuric acid and 2 of water, which has been allowed to cool, is poured upon it. 2 parts of alcohol (sp. gr. ·85) are then added, the mixture very gently heated, and the vapours condensed in a Liebig's condenser, or in a worm (fig. 196) supplied with iced water. If bichromate of potash be employed, 3 parts of the salt are introduced into the retort with 2 parts of alcohol. The retort is placed in cold water to moderate the action, and a mixture of 4 parts of sulphuric acid with three times its volume of water is allowed to flow slowly into the retort. A very gentle heat may be applied when the action has moderated.

In these processes the alcohol is oxidised according to the equation—

$$\underset{\text{Alcohol.}}{C_4H_6O_2} + O_2 = \underset{\text{Aldehyde.}}{C_4H_4O_2} + 2HO.$$

In the first process the oxygen is derived from the binoxide of manganese, leaving sulphate of manganese ($MnO.SO_3$) in the retort; in the second process, the chromic acid of the bichromate furnishes the oxygen, sulphate of chromium ($Cr_2O_3.3SO_3$) being formed. As might be expected, a portion of the alcohol is oxidised to a higher degree, and converted into acetic acid ($C_4H_4O_4$), so that some acetic ether comes over together with the aldehyde. Another product, *acetal*, is also found in the distillate, which has the composition $C_{12}H_{14}O_4$, and may be regarded as resulting from the union of 2 eqs. of ether formed by a secondary action of the sulphuric acid upon the alcohol, with 1 eq. of aldehyde ($2C_4H_5O.C_4H_4O_2$).

By redistilling the aldehyde with an equal weight of fused chloride of calcium in a gently heated water-bath, it may be freed from most of the water and alcohol, which are left behind in the retort, the boiling point of aldehyde being only 67°·8 F. For rectification, it may be separated from the acetic ether and acetal, by taking advantage of its property of combining with ammonia to form a compound which is insoluble in ether; the rectified aldehyde is mixed with twice its volume of ether, placed in a bottle surrounded by ice, and saturated with gaseous ammonia (p. 70), when white needle-like crystals of *aldehyde-ammonia* ($NH_3.C_4H_4O_2$) are deposited. By distilling this compound with diluted sulphuric acid, and condensing the vapour in a thoroughly cooled receiver, pure aldehyde is obtained, from which the last portions of water may be removed by standing over fused chloride of calcium and a second distillation.

Aldehyde may be recognised by its peculiar acrid odour, which affects the eyes, as well as by its volatility and inflammability. It absorbs oxygen from air even at the ordinary temperature, and is gradually converted into acetic acid. Its attraction for oxygen enables it to reduce the salts of silver to the metallic state, and a characteristic test for aldehyde consists in adding a little nitrate of silver and a trace of ammonia; on heating, the silver is deposited as a mirror on the sides of the test-tube. In contact with hydrate of potash, aldehyde undergoes decomposition, yielding a brown substance (resin of aldehyde) and a solution of

miate of potash. By distilling a mixture of these two salts, aldehyde reproduced—

$$\underset{\text{te of potash.}}{\ldots C_4H_3O_3} + \underset{\text{Formiate of potash.}}{KO.C_2HO_3} = 2(KO.CO_2) + \underset{\text{Aldehyde.}}{C_4H_4O_2}.$$

se reactions lend some support to the opinion, that aldehyde should resented as being framed upon the model of a molecule of hydrogen in which the place of one atom of hydrogen is occupied by *acetyle* O_2), the hypothetical radical of acetic acid. For if formiate of potash tilled with hydrate of potash, it yields carbonate of potash and two of hydrogen, $KO.C_2HO_3 + KO.HO = 2(KO.CO_2) + HH$; and etate of potash be employed instead of the hydrate, aldehyde is ned instead of hydrogen—

$$KO.C_2HO_3 + KO.(C_4H_3O_2)O = 2(KO.CO_2) + (C_4H_3O_2)H.$$

n this view it is easy to explain the tendency of aldehyde to undergo ation, both the radical, acetyle, and the hydrogen, acquiring oxygen, forming acetic acid, just as hydrogen is converted into water by oxi-on.*

Type.—Molecule of hydrogen, H . H Aldehyde (hydride of acetyle), $C_4H_3O_2 . H$	*Type.*—Molecule of water, HO . HO Acetic acid, $(C_4H_3O_2)O . HO$

As might be anticipated, it is found that when vapour of aldehyde is ssed over heated hydrate of potash (mixed with lime) it yields acetate of otash and hydrogen, $C_4H_3O_2 . H + KO . HO = H . H + KO . (C_4H_3O_2)O$.

By the action of potassium, the atom of hydrogen may be displaced from e aldehyde, and the compound $(C_4H_3O_2)K$ obtained.

In contact with water and sodium amalgam, aldehyde combines with e nascent hydrogen, and produces alcohol. Chlorine displaces three-urths of the hydrogen from aldehyde, producing *chloral*, $C_4Cl_3HO_2$, hich has been already noticed as yielding chloroform when acted on by kalies.

Perfectly pure aldehyde cannot be kept for any length of time, even in aled tubes, since it becomes converted into *metaldehyde* and *elaldehyde*, hich have the same composition as aldehyde, but differ widely from it properties, metaldehyde being a crystalline solid, and elaldehyde a liquid, oiling at 201° F. The true formula of elaldehyde would appear to be $C_{12}H_{12}O_6$, for the specific gravity of its vapour is 4·52, or three times that f aldehyde vapour (1·53). Metaldehyde is reconverted into aldehyde hen heated to 400° F. in a sealed tube.

When aldehyde is treated with a saturated solution of bisulphite of oda ($NaO . HO . 2SO_2$), it forms a crystalline compound, which is soluble n water, but insoluble in the saline solution, and contains the elements f 1 eq. of the aldehyde and 1 eq. of the bisulphite.

If the view above referred to is correct, which represents aldehyde as e hydride of acetyle (the radical of acetic acid), each of the acids belong-g to the acetic series would be expected to have a corresponding alde-yde. Accordingly, just as acetate of lime, when distilled with formiate lime, yields acetic aldehyde, so valerianic, œnanthic, and caprylic

* Aldehyde is also sometimes represented as the hydrated oxide of the hydrocarbon *signated acetyle at p. 520, when* its formula becomes $(C_4H_3)O . HO$.

aldehydes may be obtained by distilling the corresponding lime-s formiate of lime.

The chief aldehydes of this series which have at present been are—

Acetic aldehyde, . . .	$C_4H_4O_2$*
Propionic aldehyde, . .	$C_6H_6O_2$
Butyric aldehyde, . .	$C_8H_8O_2$
Valeric aldehyde, . .	$C_{10}H_{10}O_2$
Œnanthic aldehyde, . .	$C_{14}H_{14}O_2$
Caprylic aldehyde, . .	$C_{16}H_{16}O_2$
Rutic aldehyde, . . .	$C_{20}H_{20}O_2$
Euodic aldehyde, . .	$C_{22}H_{22}O_2$
Lauric aldehyde, . .	$C_{24}H_{24}O_2$

The radicals corresponding to acetyle, which may be regarded as associated with hydrogen in these aldehydes, have not, for the most part, been isolated; a substance having the same composition as butyryle, the supposed radical of butyric acid ($C_8H_8O_4$), has, however, been obtained from that acid by an indirect process.

Acetic, propionic, and butyric aldehydes have been found among the products of the oxidising action of a mixture of binoxide of manganese and sulphuric acid upon fibrine, albumen, and caseine.

Valeric aldehyde is obtained, like acetic aldehyde, by distilling the corresponding alcohol (amyle-alcohol, $C_{10}H_{12}O_2$) with sulphuric acid and bichromate of potash.

Capric (rutic), euodic, and lauric aldehydes are found in essence of rue. The higher aldehydes of the series are not so easily oxidised, containing a lower number of carbon equivalents.

When an aldehyde is heated with one of the bases derived from ammonia by the substitution of an alcohol-radical for one atom of hydrogen, the other two atoms of hydrogen of the ammonia are removed as diatomic hydrocarbon of the aldehyde; thus—

$$\underset{\text{Amylamine.}}{2NH_2C_{10}H_{11}} + \underset{\text{Œnanthic aldehyde.}}{2C_{14}H_{14}O_2} = 4HO + \underset{\text{Di-œnanthylene-}}{N_2(C_{10}H_{11})_2}$$

This reaction has been recommended for the determination of the replaceable (or typical) hydrogen in organic bases.

411. ACETONES.—If the lime salts of the acids of the series be distilled, instead of being distilled with formiate of lime, as for the production of the aldehydes, be distilled alone, or with quick-lime, a series of homologous products is obtained, each of which is isomeric with the acid of the series next below it in the table, though totally different from the aldehyde in properties.

Thus, by distilling acetate of lime with lime, the liquid acetone ($C_6H_6O_2$) is obtained, which has been already noticed among the products of the distillation of wood—

$$\underset{\text{Acetate of lime.}}{2(CaO.C_4H_3O_3)} = 2(CaO.CO_2) + \underset{\text{Acetone.}}{C_6H_6O_2}$$

Acetone has the same composition as propionic aldehyde.

* It will be remarked that these aldehydes are isomeric with the ethers formed by their acids; thus, acetic aldehyde is isomeric with acetic ether,

$$2C_4H_4O_2 = C_4H_8O.C_4H_4O_3$$

but the sp. gr. of aldehyde vapour (1·58) is only half that of acetic ether

ıe following acetones (or *ketones*, as they are frequently called) obtained :—

Acetone, . . .	$C_6H_6O_2$
Propione, . . .	$C_{10}H_{10}O_2$
Butyrone, . . .	$C_{14}H_{14}O_2$
Valerone, . . .	$C_{18}H_{18}O_2$

tances are allied, in some of their properties, to the aldehydes, in forming crystalline compounds with bisulphite of soda. ıy chemists have been led to believe that they are composed, lehydes, after the model of a molecule of hydrogen, but that in es the radicals of the corresponding acids are associated, not om of hydrogen, but with an atom of the hydrocarbon radical lower alcohol. Thus, the acetone of the acetic series ($C_6H_6O_2$) omposed of the radical acetyle ($C_4H_3O_2$) associated with methyle d this view of its constitution is supported by the formation when chloride of acetyle is acted upon by zinc-methyle—

$$\underset{\text{ride of acetyle.}}{H_3O_2.Cl} + \underset{\text{Zinc-methyle.}}{C_2H_3.Zn} = \underset{\text{Acetone.}}{C_4H_3O_2.C_2H_3} + ZnCl.$$

ıilar manner, chloracetene (resulting from the action of chloro- cid on aldehyde) yields acetone when acted on by methylate of um-methyle-alcohol)—

$$\underset{\text{loracetene.}}{(_4H_2)Cl} + \underset{\text{Methylate of soda.}}{(C_2H_3)NaO_2} = NaCl + \underset{\text{Acetone.}}{C_4H_3O_2.C_2H_3}.$$

corroboration is obtained by distilling a mixture of equivalent of acetate and valerianate of potash, when an acetone is obtained, ıtains valeryle ($C_{10}H_9O_2$), associated with methyle (C_2H_3)—

$$\underset{\text{f potash.}}{_4H_3O_3} + \underset{\text{Valerianate of potash.}}{KO.C_{10}H_9O_3} = 2(KO.CO_2) + C_{10}H_9O_2.C_2H_3.$$

e remembered that when acetate of potash is distilled with f potash, it yields marsh-gas by a precisely parallel reaction—

$$\underset{\text{ate of potash.}}{).C_4H_3O_3} + KO.HO = 2(KO.CO_2) + \underset{\text{Marsh-gas.}}{H.C_2H_3}.$$

may also be prepared by distilling sugar with eight times its quick-lime, when it is accompanied by another liquid, *metacetone*, hich differs from acetone in being insoluble in water. When d is heated with bichromate of potash and sulphuric acid, it is nd converted into *metacetonic* or *propionic acid*, $HO.C_6H_5O_3$, ıy also be produced by the oxidation of acetone.

he description above given of the properties of aldehyde will lled those of some of the essential oils containing oxygen. Thus, oil of bitter almonds ($C_{14}H_6O_2$), when exposed to air, absorbs nd is converted into benzoic acid ($C_{14}H_6O_4$), just as aldehyde passes into acetic acid ($C_4H_4O_4$). Moreover, oil of bitter forms a crystalline compound with bisulphite of soda, similar to ıed by aldehyde, and its conversion into this compound is some- orted to in order to obtain the pure oil.

nstitution, also, oil of bitter almonds (hydride of benzoyle, H) closely resembles aldehyde (hydride of acetyle, $C_4H_3O_2.H$), s *the latter may* be obtained by distilling acetate of potash with

formiate of potash, so benzoic aldehyde (oil of bitter almonds) m
obtained from benzoate of potash—

$$\underset{\text{Benzoate of potash.}}{KO.(C_{14}H_5O_2)O} + \underset{\text{Formiate of potash.}}{KO.C_2HO_3} = 2(KO.CO_2) + \underset{\text{Benzoic alde}}{C_{14}H_6O_2}$$

Oil of bitter almonds is produced, together with some aldehydes
acetic series of acids (p. 556), when certain albuminous bodies ar
dised by sulphuric acid and binoxide of manganese.

When benzoic aldehyde is acted on by an alcoholic solution of h
of potash, an oily liquid is obtained, which stands in the same rela
benzoic aldehyde as alcohol bears to acetic aldehyde—

$$\underset{\text{Benzoic aldehyde.}}{2(C_{14}H_5O_2.H)} + KO.HO = \underset{\text{Benzoate of potash.}}{KO.(C_{14}H_5O_2)O} + \underset{\text{Benzoic alco}}{C_{14}H_6O_2}$$

The hydrochloric ether of benzoic alcohol, $C_{14}H_7Cl$, is sometimes
chloride of benzyle, the radical *benzyle*, $C_{14}H_7$, being supposed to ha
same relation to the benzoic series as ethyle has to the acetic series
the action of ammonia upon chloride of benzyle, *benzylamine*, $NH_2($
and *tri-benzylamine*, $N(C_{14}H_7)_3$, have been obtained; the former is is
with toluidine, but is by no means identical with it, for benzylamin
liquid having basic properties far more powerful than those of
dine, and it is very readily soluble in water, which dissolves but l
the latter base.

The benzoic acetone or *benzone* ($C_{26}H_{10}O_2$) has been obtained by th
lation of benzoate of lime. It is often called *benzophenone*, being rega
an association of benzoyle with phenyle, $C_{14}H_5O_2.C_{12}H_5$; for when i
with hydrate of potash, it yields benzoate of potash and benzole (h
of phenyle)—

$$\underset{\text{Benzophenone.}}{C_{14}H_5O_2.C_{12}H_5} + KO.HO = \underset{\text{Benzoate of potash.}}{KO.(C_{14}H_5O_2)O} + \underset{\text{Benzol}}{C_{12}H_6}$$

Oil of cinnamon (p. 476) or hydride of cinnamyle ($C_{18}H_7O_2.H$
aldehyde of cinnamic acid ($C_{18}H_8O_4$); and essential oil of cummin
the aldehyde ($C_{20}H_{11}O_2.H$) of cuminic acid ($C_{20}H_{12}O_4$), and yields
alcohol ($C_{20}H_{14}O_2$) when treated with alcoholic solution of potash.
spiræa or hydride of salicyle ($C_{14}H_5O_4.H$) is the aldehyde of salic
($C_{14}H_6O_6$). Hydride of anisyle ($C_{16}H_7O_4.H$), obtained by the
of oil of aniseed, is the aldehyde of anisic acid ($C_{16}H_8O_6$), and
alcohol ($C_{16}H_{10}O_2$). These aldehydes allow their associated atom
gen to be displaced by chlorine more readily than the aldehyd
acetic series, to form chlorides of their respective radicals (p. 475

Glycol—Polyatomic Alcohols.

413. It has been already shown (p. 526) that alcohol may
veniently regarded as composed after the fashion of a molecule
($H_2\Theta$) in which half the hydrogen has been displaced by ethyl
according to this view alcohol is represented by the molecula
$H(\Theta_2H_5)\Theta$; and it is a *monatomic* alcohol, for it contains the m
radical $(\Theta_2H_5)'$. But if, following the same plan, a diatomic rad
as ethylene $(C_4H_4)''$, were to displace half the hydrogen in wate
placement could not be effected in less than two molecules of wat
and a *diatomic alcohol* would result.

Glycol ($C_4H_6O_4$) is the representative of the diatomic alcohols
be regarded as four equivalents of water, in which half the hy
replaced by ethylene ($H_2(C_4H_4)''O_2$). It is obtained by the

iodide of ethylene (formed by the direct union of olefiant gas with ine) upon acetate of silver—

$$(AgO.C_4H_3O_3) + (C_4H_4)''I_2 = 2AgI + (C_4H_4)''O_2.2C_4H_3O_3.$$

Acetate of silver. Biniodide of ethylene. Binacetate of glycol.

e binacetate of glycol thus formed corresponds to the acetic ether $_4H_3)O.C_4H_3O_3$) derived from common alcohol; but since glycol is tomic, it combines with two equivalents of acetic acid. When the alt of this action is distilled, the binacetate of glycol passes over as a ourless liquid, which sinks in water, and boils at 365° F.*

Glycol can be obtained from the binacetate by digesting it with hydrate potash for some time at 360° F., and distilling, when the glycol passes er, its boiling point being 387° F. It is a colourless liquid, having a eet taste, whence it derives its name (γλυκύς, *sweet*). Like common ohol, it mixes with water in all proportions, and may be distilled thout decomposition. It also gives an inflammable vapour, and has ver been frozen; but, unlike alcohol, it is heavier than water (sp. gr. 25), and does not mix with ether, though alcohol dissolves it readily.

Glycol is also capable of uniting with one equivalent of acetic acid, ming the *monacetate of glycol*, $C_4H_4O_2.HO.C_4H_3O_3$, and a remarkable mpound has been obtained containing glycol in combination with etic and butyric acids; this *acetobutyrate of glycol* has the composition $H_2O_2.C_4H_3O_3.C_8H_7O_3$.

The action of hydrochloric acid upon glycol does not perfectly corres nd with its action upon common alcohol, for instead of yielding a chlo- de of ethylene, it gives a compound of hydrochloric acid with oxide of hylene—

$$H_2(C_4H_4)''O_4 + HCl = (C_4H_4)''O_2.HCl + 2HO.$$

Glycol. Chlorhydrine of glycol.

y decomposing this compound with potash, the binoxide of ethylene $_4H_4)''O_2$ is obtained, as a colourless liquid, which boils at 56° F., and is, erefore, not identical with aldehyde (which boils at 68° F.), though it as the same composition. It is obvious that glycol might be represented s $(C_4H_4)''O_2.2HO$, the hydrated binoxide of ethylene, and this view is voured by the circumstance that glycol may be formed by heating the inoxide of ethylene with water in a sealed tube; but, on the other hand, hen glycol is treated with chloride of zinc, to dehydrate it, ordinary alde- yde ($C_4H_4O_2$), and not the ethylenic binoxide, is produced.

By the action of pentachloride of phosphorus upon glycol, the bichloride of ethylene, or Dutch liquid, is obtained—

$$H_2(C_4H_4)''O_4 + 2PCl_5 = (C_4H_4)''Cl_2 + 2HCl + 2PO_2Cl_3.$$

Glycol. Bichloride of ethylene. Oxychloride of phosphorus.

It will be observed that this equation is the exact counterpart of that which represents the action of pentachloride of phosphorus upon water, substituting diatomic ethylene for monatomic hydrogen—

$$H_2(H_2)''O_4 + 2PCl_5 = (H_2)''Cl_2 + 2HCl + 2PO_2Cl_3.$$

Sodium acts upon glycol in the same manner as upon ordinary alcohol, but in consequence of the di-atomic character of glycol, the reaction

* A liquid isomeric with binacetate of glycol, but boiling at 336° F., is obtained by heating *aldehyde in a sealed tube with* acetic anhydride.

takes place in two stages, producing, successively, *mono-sodium gly* $HNa(C_4H_4)''O_4$, and *di-sodium glycol*, $Na_2(C_4H_4)''O_4$, both which are

When glycol is exposed to the action of oxygen in the presence platinum-black, or when it is cautiously oxidised with nitric acid, it comes converted into *glycolic acid*, $C_4H_4O_6$, which bears the same relation to it as acetic acid bears to common alcohol, as will be evident from the following equations:*—

$$\underset{\text{Alcohol.}}{H(C_4H_5).O_2} + O_4 = \underset{\text{Acetic acid.}}{H(C_4H_3O_2).O_2} + 2HO$$

$$\underset{\text{Glycol.}}{H_2(C_4H_4)''.O_4} + O_4 = \underset{\text{Glycolic acid.}}{H_2(C_4H_2O_2)''.O_4} + 2HO$$

in which the change consists, in both cases, in the substitution of O_2 H_2 in the radical of the alcohol, acetic acid being formed upon the type of two equivalents of water (H_2O_2) in which H is replaced by C_4H_3, and glycolic acid upon the type of four equivalents (H_4O_4), in which are replaced by $C_4H_2O_4$. If the oxidation with nitric acid be carried farther, the remainder of the hydrogen in this last radical is replaced by oxygen, and oxalic acid is produced—

$$\underset{\text{Glycolic acid.}}{H_2(C_4H_2O_2)''.O_4} + O_2 = \underset{\text{Oxalic acid.}}{H_2(C_2O_4)''.O_4} + 2HO.$$

By the action of nascent hydrogen upon oxalic acid, the O_2 in the radical may be again displaced by H_2, so that glycolic acid is reproduced.

Glycolic acid forms a syrupy liquid which resembles lactic acid, but is distinguished from it by being precipitated with acetate of lead. Unlike oxalic acid, glycolic is a monobasic acid, only one equivalent of its hydrogen being replaceable by a metal. Glycolic acid is found together with oxalic acid among the products of the action of nitric acid upon alcohol in the preparation of fulminate of mercury, which is easily accounted for by the connection between alcohol and ethylene, which is best exhibited by writing the formula of alcohol $(C_4H_4).2HO$.

Glycolic acid is the first member of a series of homologous acids of which the most important is lactic acid, these acids standing in the same relation to the glycols in which the members of the acetic series stand to the alcohols.

Lactic Series of Acids.

Name.	Equivalent Formula.	Source.
Glycolic acid, .	$C_4H_4O_6$	Oxidation of glycol and of alcohol.
Lactic acid, .	$C_6H_6O_6$	Fermentation of cane and milk sugar.
Butylactic acid, .	$C_8H_8O_6$	Oxidation of butyl-glycol.
Valerolactic acid,	$C_{10}H_{10}O_6$	Decomposition of bromo-valerianic acid with oxide of silver.
Leucic acid, .	$C_{12}H_{12}O_6$	Action of nitric acid on leucine.

It will be observed that these acids are intermediate, with respect to the number of equivalents of oxygen which they contain, between the acetic and the oxalic series of acids; thus—

Acetic acid,	.	$C_4H_4O_4$	Propionic acid,	.	C_6
Glycolic ,,	.	$C_4H_4O_6$	Lactic ,,	.	C_6
Oxalic ,,	.	$C_4H_2O_8$	Malonic ,,	.	C_6

* The aldehyde of glycol, glycoxal, $C_4H_4O_4$, is found among the products of the decomposition of nitrous ether in contact with water.

se three series of acids, therefore, present a relation to each other to that between the three series of alcohols, represented by—

Vinic alcohol, . .	$C_4H_6O_2$
Glycol, . . .	$C_4H_6O_4$
Glycerine, . .	$C_6H_8O_6$

as acetic and glycolic acids are formed by the oxidation of alcohol ycol, so the oxidation of glycerine by nitric acid furnishes *glyceric* $C_6H_6O_8$.

transition from the oxalic series to the lactic series of acids has ffected in the case of leucic acid, which has been artificially formed xalic acid, by converting it into oxalic ether, and acting upon this inc-ethyle, when leucic ether is obtained, from which leucic acid is prepared. The reaction is rendered intelligible if the two acids be ormulated—

Oxalic acid, . .	$C_4H_2O_8$
Leucic ,, . .	$C_4H_2(C_4H_5)_2O_6$

which it appears that, neglecting intermediate stages, the zinc of the hyle removes two equivalents of oxygen from the oxalic acid, leav- o equivalents of ethyle in their stead, so that leucic acid may be ed as *diethoxalic acid*, or oxalic acid containing two equivalents of instead of two equivalents of oxygen. If oxalate of methyle be tuted for oxalate of ethyle in this experiment, leucate of methyle,). $C_{12}H_{11}O_5$, is obtained, and when this is decomposed by baryta, and ucate of baryta treated with sulphuric acid, fine crystals of leucic re obtained which are readily soluble in water, alcohol, and ether, ublime slowly at the ordinary temperature.* By the reaction be- iodide of methyle, oxalate of methyle, and amalgamated zinc, *oxalic acid*, $C_4H_2(C_2H_3)_2O_6$, has been obtained, which may be re- l as oxalic acid containing two equivalents of methyle in the place o equivalents of oxygen. Dimethoxalic acid is isomeric with buty- or acetonic acid ($C_5H_8O_6$); it crystallises in prisms resembling those alic acid, which may be sublimed at 122° F., and volatilise slowly t the ordinary temperature.

m the other hydrocarbons of the olefiant gas series (p. 515), glycols e prepared by processes similar to that which furnishes ethylene- . Thus propylene (C_6H_6) yields *propylene-glycol*, $H_2(C_6H_6)''.O_4$; ne (C_8H_8), *butylene-glycol*, $H_2(C_8H_8)''.O_4$; amylene ($C_{10}H_{10}$), *amy- ycol*, $H_2(C_{10}H_{10})''.O_4$; it is a very remarkable circumstance that the g points and specific gravities of these liquids *decrease* as the com- y of the formula *increases*, which is quite contrary to ordinary ence; thus amylene-glycol ($C_{10}H_{12}O_4$) has the sp. gr. 0·987, and t 351° F., whilst propylene-glycol ($C_6H_8O_4$) has the sp. gr. 1·051, oils at 371° F.

en propylene-glycol is slowly oxidised, it is converted into *lactic* exactly as glycol is converted into glycolic acid—

$$\underset{\text{Propylene-glycol.}}{H_2(C_6H_6)''.O_4} + O_4 = \underset{\text{Lactic acid.}}{H_2(C_6H_4O_2)''.O_4} + 2HO.$$

difference between the diatomic character of glycol and the mona-

* It is said that this leucic acid, though closely resembling that obtained from oxalic acid, is *not identical with it.*

tomic character of ordinary alcohol, is strongly marked in their b... with the organic acids, for whilst the monatomic alcohol yields (... monobasic acids) only one series of compound ethers containing one ... valent of acid, the diatomic glycol yields two series containing respe... one and two equivalents of acid; thus we have monacetate of gl... $(C_4H_4)''O_2 . HO . C_4H_3O_3$, and binacetate of glycol, $(C_4H_4)''O_2 . 2C_4$... In the last series, it is not necessary that the two equivalents should ... sist of the same acid, as may be seen in the acetobutyrate of gl... $(C_4H_4)''O_2 . C_4H_3O_3 . C_8H_7O_3$, in which the glycol is combined with ... and butyric acids.

Just as polyatomic ammonias are formed upon the type of several ... of ammonia, so polyatomic alcohols may be produced by the substi... of compound radicals for hydrogen in a multiple alcohol type. Thus, ... heating glycol in a sealed tube with binoxide of ethylene, *di-ethyl... trialcohol*, $H_3(C_2H_4)''_2O_3$, is produced, which is formed upon the type ... three molecules of alcohol, $H_3(C_2H_5)_3O_3$. In a similar manner, tri-eth... lene-tetralcohol, $H_2(C_2H_4)_3''O_4$, is formed upon the quadruple alcohol typ... $H_4(C_2H_4)_4O_4$.

It will be seen hereafter that glycerine ($C_6H_8O_6$), the sweet principle ... oils and fats, is a triatomic alcohol, formed upon the type of three mol... cules of water (H_6O_3), in which half the hydrogen is replaced by th... triatomic radical, $(C_3H_5)'''$, *glyceryle*, the molecular formula of glycer... being $H_3(C_3H_5)'''O_3$.

It is easy to convert a diatomic into a monatomic alcohol; for exampl... if the chlorhydrine of glycol be treated with amalgam of sodium in t... presence of water, it becomes converted into ordinary (monatomic) alcohol.

$$\underset{\text{Chlorhydrine of glycol.}}{C_4H_5ClO_2} + HO + Na_2 = \underset{\text{Alcohol.}}{C_4H_6O_2} + NaO + NaCl.$$

The relation of the alcohols to water as their primary type is h... exhibited—

Type, one molecule of water, H_2O_2 = $\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$

Vinic alcohol, $C_4H_6O_2$ = $\left.\begin{matrix}H\\(C_4H_5)'\end{matrix}\right\}O_2$

Type, two molecules of water, H_4O_4 = $\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_4$

Glycol, $C_4H_6O_4$ = $\left.\begin{matrix}H_2\\(C_4H_4)''\end{matrix}\right\}O_4$

Type, three molecules of water, H_6O_6 = $\left.\begin{matrix}H_2\\H_2\\H_2\end{matrix}\right\}O_6$

Diethylene-trialcohol, $C_8H_{10}O_6$ = $\left.\begin{matrix}H_3\\(C_4H_4)''\\(C_4H_4)''\end{matrix}\right\}O_6$

Glycerine, $C_6H_8O_6$ = $\left.\begin{matrix}H_3\\(C_6H_5)'''\end{matrix}\right\}O_6$

Type, four molecules of water, H_8O_8 = $\left.\begin{matrix}H_2\\H_6\end{matrix}\right\}O_8$

Triethylene-tetralcohol, $C_{12}H_{14}O_8$ = $\left.\begin{matrix}H_2\\(C_6H_5)''_2\end{matrix}\right\}O_8$

compounds formed by the action of acids upon these alcohols would e represented by such formulæ as the following :—

Acetic ether, ...	$\left.\begin{matrix}(C_4H_3O_2)'\\(C_4H_5)'\end{matrix}\right\}O_2$
Monacetate of glycol, . .	$\left.\begin{matrix}(C_4H_3O_2)'H\\(C_4H_4)''\end{matrix}\right\}O_4$
Binacetate of glycol, . .	$\left.\begin{matrix}(C_4H_3O_2)_2'\\(C_4H_4)''\end{matrix}\right\}O_4$
Acetobutyrate of glycol,	$\left.\begin{matrix}(C_4H_3O_2)'\\(C_8H_7O_2)'\\(C_4H_4)''\end{matrix}\right\}O_4$
Monacetine, ...	$\left.\begin{matrix}(C_4H_3O_2)'H_2\\(C_6H_5)'''\end{matrix}\right\}O_6$
Diacetine, ...	$\left.\begin{matrix}(C_4H_3O_2)_2'H\\(C_6H_5)'''\end{matrix}\right\}O_6$
Triacetine, ...	$\left.\begin{matrix}(C_4H_3O_2)_3'\\(C_6H_5)'''\end{matrix}\right\}O_6$

ACETIC ACID—THE FATTY ACID SERIES.

The most useful of the acids belonging to the acetic series (*see*) is acetic acid itself, the preparation of which has been already de-

.

y of its salts are extensively employed in the arts. *Acetate of a* ($Al_2O_3 . 3C_4H_3O_3$) is used as a mordant by the dyer and calico- . *Acetate of lead* or *sugar of lead* ($PbO . C_4H_3O_3, 3Aq.$) is pre- y dissolving litharge (PbO) in an excess of acetic acid, when the n deposits prismatic crystals of the acetate which are easily dis- by water and alcohol.

Iard's extract, or *tribasic acetate of lead*, is prepared by dissolving e in solution of acetate of lead ; it may be obtained in needle-like s, which have the composition ($3PbO . C_4H_3O_3, HO$).

ligris, or *basic acetate of copper* ($2CuO . C_4H_3O_3, 6HO$), is prepared ng up sheets of copper with layers of fermenting husks of grapes rc of the wine-press), when the oxide of copper, formed at the ex- of the oxygen of the air, combines with the acetic acid furnished oxidation of the alcohol.

ne ($C_6H_6O_2$) is obtained by the destructive distillation of acetate —

$$\underset{\text{Acetate of lime.}}{2(CaO . C_4H_3O_3)} = 2(CaO . CO_2) + \underset{\text{Acetone.}}{C_6H_6O_2}$$

nposition which possesses some general interest since the lime-salts other acids of the acetic series yield *ketones* in a similar manner 556).

acetone thus obtained is an ethereal liquid lighter than water, boil- 133° F., and burning with a luminous flame. It is easily miscible ater, but separates when hydrate of potash is added, rising to the

er the action of chlorine, acetic acid loses an atom of hydrogen, chlorine in its place, and forming *chloracetic acid*, $HO . C_4H_2ClO_3$;*

* *Bichloracetic acid*, $HO . C_4HCl_2O_3$, has recently been obtained.

and if the action be promoted by sun-light, *trichloracetic acid* may be formed, $HO.C_4Cl_3O_3$, which may be crystallised. This latter acid has a peculiar interest on account of its being concerned in the production of acetic acid from inorganic materials, which was one of the first examples of the actual synthesis of organic compounds.

By passing vapour of sulphur over red-hot carbon, bisulphide of carbon, CS_2, is formed. When this is boiled with a mixture of hydrochloric and nitric acids, a white crystalline substance is obtained, which contains $CSCl_2O_2$. By passing the vapour of this substance through a red-hot tube it suffers decomposition, and liquid protochloride of carbon, C_4Cl_4, is found among the products—

$$4CSCl_2O_2 = C_4Cl_4 + Cl_4 + 4SO_2.$$

By exposing this chloride of carbon, in the presence of water, to the action of chlorine encouraged by sunlight, trichloracetic acid is obtained—

$$C_4Cl_4 + 4HO + Cl_2 = HO.C_4Cl_3O_3 + 3HCl.$$

By acting upon the solution of trichloracetic acid with amalgam of potassium, acetate of potash is formed—

$$\underset{\text{Trichloracetic acid.}}{HO.C_4Cl_3O_3} + K_2 + 4HO = \underset{\text{Acetate of potash.}}{KO.C_4H_3O_3} + 2(KO.HO) + 3KCl.$$

From the acetate of potash, of course, acetic acid is readily obtained.

The synthesis of acetic acid has been effected in a simpler manner by the action of chlorocarbonic acid upon marsh-gas, when hydrochloric acid and acetic oxychloride are formed—

$$C_2H_4 + 2COCl = \underset{\text{Acetic oxychloride.}}{(C_4H_3O_2)Cl} + HCl.$$

When the acetic oxychloride is decomposed by water, acetic acid is produced—

$$(C_4H_3O_2)Cl + 2HO = HO.C_4H_3O_3 + HCl.$$

This appears to be an example of a general method of synthesis of the volatile fatty acids, starting from the marsh-gas hydrocarbons derived from them; thus, hydride of amyle, $C_{10}H_{12}$, treated in a similar manner, yields caproic acid, $HO.C_{12}H_{11}O_3$.

415. *Anhydrides of organic acids—Acetic anhydride.*—The course of investigation by which, of late years, much light has been thrown upon the true constitution of acetic acid, and therefore of many other organic acids, is of a very instructive character. The strongest acetic acid which can be prepared (*see* p. 466) is known as *glacial acetic acid*, from its crystallising in icy leaflets at about 55° F. This acid has the composition $C_4H_4O_4$; but if it be neutralised with carbonate of soda, the acetate of soda obtained has the formula $NaO.C_4H_3O_3$, showing that the elements of an equivalent of water have been removed from the acid in the act of combining with the soda. This has led chemists to regard ordinary acetic acid as *hydrated acetic acid*, a compound of water with *anhydrous acetic acid*, $C_4H_3O_3$; but all attempts to obtain this body by the abstraction of water from acetic acid have failed entirely. The application of the principle of substitution or displacement, however, has brought this substance to light.

When acetic acid is distilled with terchloride of phosphorus, a colourless, very pungent liquid is obtained, which is commonly spoken of as *acetic oxychloride*, $C_4H_3O_2Cl$, and may be regarded as the anhydrous acetic acid from which one equivalent of oxygen has been removed, the vacancy being filled up by an equivalent of chlorine—

$$2[HO.(C_4H_3O_2)O] + PCl_3 = HO + HCl + PO_3 + 2[(C_4H_3O_2)Cl].$$
Acetic acid. Acetic oxychloride.

That this acetic oxychloride (or *chloride of acetyle*) really bears a very close relationship to acetic acid, and is, in fact, composed after the same type, is shown by the action of water, which at once reproduces the acetic acid, exchanging its oxygen for the chlorine of the oxychloride—

$$(C_4H_3O_2)Cl + 2HO = HO.(C_4H_3O_2)O + HCl$$
Acetic oxychloride. Acetic acid.

but the $C_4H_3O_3$ thus formed combines immediately with an equivalent of water to form the hydrated acetic acid. The action takes place with explosive violence.

If hydrate of potash be allowed to act upon the chloride of acetyle, it is the potash which exchanges its oxygen for the chlorine, whilst the water, as before, enters into combination with the $C_4H_3O_3$—

$$(C_4H_3O_2)Cl + KO.HO = HO.(C_4H_3O_2)O + KCl.$$

But if acetate of potash ($KO.C_4H_3O_3$) be employed instead of hydrate of potash, the potash still exchanges its oxygen for the chlorine; but the $C_4H_3O_3$ with which it was combined, enters into combination with the $C_4H_3O_3$ formed during the reaction, and thus produces a double atom of the radical supposed to exist in acetic acid, and commonly spoken of as *acetic anhydride*—

$$(C_4H_3O_2)Cl + KO.C_4H_3O_3 = C_4H_3O_3.C_4H_3O_3 + KCl.$$
Acetic oxychloride. Acetate of potash. Acetic anhydride.

Acetic anhydride has also been obtained by heating dry acetate of lead or of silver with bisulphide of carbon in a sealed tube to about 320° F. for several hours, the tube being occasionally opened to relieve the pressure of the carbonic acid evolved—

$$2(PbO.C_4H_3O_2) + CS_2 = 2PbS + CO_2 + 2(C_4H_3O_2).$$

The acetic anhydride is a neutral oily liquid which may be distilled off in the above experiment. Its smell recalls that of acetic acid, but affects the eyes strongly. It sinks in water, but dissolves slowly, with evolution of heat and formation of hydrated acetic acid.*

The most convincing proof that this anhydride is really an association of two atoms (each representing two volumes of vapour (O = 1 volume)) is obtained by acting upon the acetate of potash with the benzoic instead of the acetic oxychloride, when a benzo-acetic anhydride is formed, con-

* If acetic anhydride be heated with an excess of binoxide of barium, it yields acetate of baryta, carbonic acid, and methyle gas (p. 519).

$$2(C_4H_3O_3) + BaO_2 = BaO.C_4H_3O_3 + C_2H_3 + 2CO_2.$$

By absorbing the carbonic acid with potash, the pure methyle gas is easily obtained.

taining benzoic anhydride ($C_{14}H_5O_2$) in combination with acetic anhydride ($C_4H_3O_2$)—

$$\underset{\text{Benzoic oxychloride.}}{(C_{14}H_5O_2)Cl} + \underset{\text{Acetate of potash.}}{KO.C_4H_3O_2} = KCl + \underset{\text{Benzo-acetic anhydride.}}{C_{14}H_5O_2.C_4H_3O_2}$$

and the true nature of this double anhydride is seen by its conversion into a mixture of hydrated benzoic and acetic acids when left in contact with water.

By methods similar to that employed for acetic acid, the anhydrides of many other organic acids may be obtained, being thus removed from the list of hypothetical compounds to take their places among recognised forms of combination.

The mode of formation of these anhydrides, however, occasions serious doubt as to the propriety of regarding the acids in their ordinary form as hydrates, or compounds containing water. If acetic acid, for example, is really a hydrate of the radical $C_4H_3O_2$, why are we unable to remove the water by the application of some dehydrating agent, instead of having recourse to the above circuitous process? The answer appears to be, that the acetic anhydride is really formed by a process of substitution, and is not to be regarded as pre-existent in the ordinary acetic acid.

Ordinary acetic acid may, with great advantage for explaining many points in its history, be regarded as composed after the type of two equivalents of water in which half the hydrogen is replaced by the compound group $C_4H_3O_2$—

$$HO.C_4H_3O_2 = \left.\begin{matrix} C_4H_3O_2 \\ H \end{matrix}\right\} O_2.$$

The composition of the acetic oxychloride ($C_4H_3O_2Cl$), and of acetamide $NH_2.C_4H_3O_2$, speaks strongly in favour of this view.

Acetate of potash would then be represented by the formula—

$$\left.\begin{matrix} C_4H_3O_2 \\ K \end{matrix}\right\} O_2 = KO.C_4H_3O_2$$

being formed from acetic acid by the substitution of potassium for hydrogen; and if we represent hydrate of potash upon the water-type, its behaviour with acetic acid would be thus expressed—

$$\underset{\text{Hydrate of potash.}}{\left.\begin{matrix} K \\ H \end{matrix}\right\} O_2} + \underset{\text{Acetic acid.}}{\left.\begin{matrix} C_4H_3O_2 \\ H \end{matrix}\right\} O_2} = \underset{\text{Acetate of potash.}}{\left.\begin{matrix} C_4H_3O_2 \\ K \end{matrix}\right\} O_2} + \underset{\text{Water.}}{\left.\begin{matrix} H \\ H \end{matrix}\right\} O_2}.$$

The formation of the double anhydride by the action of the acetate of potash upon acetic oxychloride, would then consist simply in the substitution of the $C_4H_3O_2$ in the latter for the K in the former—

$$\underset{\text{Acetate of potash.}}{\left.\begin{matrix} C_4H_3O_2 \\ K \end{matrix}\right\} O_2} + \underset{\text{Acetic oxychloride.}}{C_4H_3O_2.Cl} = \underset{\text{Acetic anhydride.}}{\left.\begin{matrix} C_4H_3O_2 \\ C_4H_3O_2 \end{matrix}\right\} O_2} + KCl$$

and, upon the same principles, the formation of the benzo-acetic anhydride would be thus represented—

$$\underset{\text{Acetate of potash.}}{\left.\begin{matrix} C_4H_3O_2 \\ K \end{matrix}\right\} O_2} + \underset{\text{Benzoic oxychloride.}}{C_{14}H_5O_2.Cl} = \underset{\text{Benzo-acetic anhydride.}}{\left.\begin{matrix} C_4H_3O_2 \\ C_{14}H_5O_2 \end{matrix}\right\} O_2} + KCl.$$

Peroxides of organic radicals.—Considerable support has been offered to this view of the constitution of the organic acids, by the discovery of certain compounds which bear the same relation to the anhydrides as binoxide of hydrogen bears to water.

When binoxide of barium is acted on by hydrochloric acid, chloride of barium and binoxide of hydrogen are formed—

$$BaO_2 + HCl = BaCl + HO_2 .$$

If binoxide of barium be acted on by benzoic oxychloride (chloride of benzoyle), the products are chloride of barium and *benzoic peroxide* (binoxide of benzoyle)—

$$BaO_2 + (C_{14}H_5O_2)Cl = BaCl + (C_{14}H_5O_2)O_2 .$$

The benzoic peroxide may be obtained in fine crystals from its ethereal solution, but like the binoxide of hydrogen, it is easily decomposed at about 212° F. with explosive violence. By the action of alkalies, it is resolved into benzoic acid and oxygen, just as binoxide of hydrogen yields water and oxygen—

$$(C_{14}H_5O_2)O_2 + KO = KO.(C_{14}H_5O_2)O + O .$$

By acting upon acetic anhydride with binoxide of barium, the *acetic peroxide* (or binoxide of acetyle) is obtained—

$$BaO_2 + 2(C_4H_3O_2)O = \underset{\text{Acetate of baryta.}}{BaO.(C_4H_3O_2)O} + \underset{\text{Acetic peroxide.}}{(C_4H_3O_2)O_2} .$$

The acetic peroxide is an oily liquid, insoluble in water, and exploding with great violence when heated. It has the powerful oxidising properties which would be expected from its chemical resemblance to binoxide of hydrogen. The true relationship between these substances is best seen in their *atomic* formulæ—

$$\underset{\text{Water.}}{H_2\Theta} ; \quad \underset{\text{Hydric peroxide.}}{H_2\Theta_2} ; \quad \underset{\text{Acetic anhydride.}}{(\Theta_2H_3\Theta)_2\Theta} ; \quad \underset{\text{Acetic peroxide.}}{(\Theta_2H_3\Theta)_2\Theta_2} .$$

416. *Formic acid* ($HO.C_2HO_3$) is regarded with great interest by the chemist, from its occurring both in the animal and vegetable kingdoms, and from the ease with which it may be artificially obtained. This acid is found in the leaves of stinging-nettles, and was originally obtained by distilling the red ants (*formica rufa*), whence it derives its name.

It has long been prepared in laboratories by the oxidation of various organic substances, particularly by distilling starch with binoxide of manganese and sulphuric acid. Another more modern process, which yields it more abundantly, consists in distilling dried oxalic acid with enough glycerine to cover it, in a water-bath, when it is resolved into carbonic acid and formic acid—

$$\underset{\text{Oxalic acid.}}{2(HO.C_2O_3)} = \underset{\text{Formic acid.}}{HO.C_2HO_3} + 2CO_2 .$$

The glycerine appears to act by producing an unstable compound with the formic acid (analogous to the stearines and acetines, *see* p. 575), which is afterwards decomposed. The solution of formic acid thus obtained contains 75 per cent. of true hydrated formic acid. If dried oxalic acid be heated in the aqueous formic acid, and the solution allowed to crystallise, the oxalic acid retains the water, and when the liquid is decanted from

the crystals and distilled, pure hydrated formic acid is obtained, and m be crystallised at a low temperature.

But the most remarkable method of obtaining formic acid is that which it is formed from inorganic materials. When formic acid is hea with strong sulphuric acid, it is resolved into water and carbonic ox $HO.C_2HO_3 = 2HO + 2CO$.

It might, therefore, be expected to be reproducible by the combinatio those two substances, and accordingly, if moistened hydrate of potas heated for some hours to 212° F. in a flask filled with carbonic oxide gas is absorbed, and formiate of potash produced, from which the fo acid may be obtained by distillation with diluted sulphuric acid—

$$KO.HO + 2CO = \underset{\text{Formiate of potash.}}{KO.C_2HO_3}.$$

This is a far simpler example of the synthesis of an organic comp from inorganic materials than that of acetic acid above referred to since the carbonic oxide may be prepared by heating carbonate of l with metallic iron, this method of synthesis is quite independent o organic source of carbon. Ethylate of soda, $NaO.C_4H_5O$, also a carbonic oxide, forming *ethyl-formiate of soda*, $NaO.C_2(C_4H_5)O_3$, is with propionate of soda, a little of this salt being also formed.

In properties, formic acid bears a great general resemblance to acid, but has a more powerful action upon the skin when in the c trated form.

Furfurole ($C_{10}H_4O_4$), or oil of ants, accompanies the formic acid obtained tilling amylaceous matters with binoxide of manganese and sulphuric aci prepared in quantity by distilling bran (freed from starch and gluten by in a cold weak solution of potash) with half its weight of sulphuric acid (pr diluted with an equal bulk of water), a current of steam being forced thro mixture; the furfurole distils over with the water, from which it may be s by fractional distillation. It is a colourless oily substance smelling of bitter a becoming brown when exposed to the air, and but slightly soluble in water. sulphuric acid dissolves it to a purple liquid, from which water precipitat changed. Furfurole resembles the aldehydes in its property of reducing silver, and in forming a crystalline compound with bisulphite of soda. I vertible by oxidation into pyromucic acid ($C_{10}H_4O_6$), the acid obtained by d the mucic acid derived from the oxidation of gum or milk-sugar. The sy name for furfurole, therefore, would be *pyromucic aldehyde*.

Just as oil of bitter almonds (benzoic aldehyde), when acted on by amm converted into hydrobenzamide, so furfurole yields *furfuramide*—

$$\underset{\text{Oil of bitter almonds.}}{3C_{14}H_6O_2} + 2NH_3 = \underset{\text{Hydrobenzamide.}}{C_{42}H_{18}N_2} + 6HO$$

$$\underset{\text{Furfurole.}}{3C_{10}H_4O_4} + 2NH_3 = \underset{\text{Furfuramide.}}{C_{30}H_{12}N_2O_6} + 6HO.$$

And, just as hydrobenzamide, when boiled with solution of potash, yields meric base *amarine* or *benzoline* ($C_{42}H_{18}N_2$), so furfuramide, when boiled with gives *furfurine* ($C_{30}H_{12}N_2O_6$), which is isomeric with it.

Butyric acid ($HO.C_8H_7O_3$) is found not only in rancid butter, the juice of muscular flesh, and is a frequent product of fermen Indeed, the best mode of obtaining this acid consists in exciting f tation in sugar by contact with cheese; the liquid soon becomes consequence of the formation of *lactic acid* (the acid of sour milk), it be neutralised from time to time with chalk, this fermentation co until the whole is converted into a pasty crystalline mass of lac

ne ($CaO.C_6H_5O_5$). The formation of lactic acid from sugar becomes intelligible on comparing the formulæ—

1 equivalent of cane-sugar, $C_{12}H_{11}O_{11}$
2 equivalents of lactic acid, $C_{12}H_{12}O_{12}$

After a time the mass becomes more fluid, at the same time evolving bubbles of gas, which contain carbonic acid and hydrogen, for the lactate of lime is undergoing a fermentation, by which it is converted into butyrate of lime—

$$2(CaO.C_6H_5O_5) + HO = CaO.C_8H_7O_3 + CaO.CO_2 + 3CO_2 + H_4.$$
Lactate of lime. Butyrate of lime.

By distilling the butyrate of lime with dilute hydrochloric acid, an aqueous solution of butyric acid is obtained, and on saturating this with chloride of calcium, the acid collects as an oily layer upon the surface. It is remarkable for its powerful odour of rancid butter.*

Synthetical formation of acids of the acetic series.—By a very remarkable process of substitution, butyric acid has been derived from acetic acid. When sodium is heated with acetic ether, it is gradually dissolved, with disengagement of hydrogen, and the liquid solidifies on cooling, to a crystalline mass of *sodacetic ether*, or acetic ether in which one atom of the hydrogen has been displaced by sodium—

$$C_4H_3O.C_4H_3O_3 + Na = C_4H_3O.C_4(H_2Na)O_3 + H.$$
Acetic ether. Sodacetic ether.

By digesting the sodacetic ether with iodide of ethyl for several hours in a close vessel, at 212° F., the atom of sodium is exchanged for ethyle, and *ethacetic ether*, or butyric ether, is produced—

$$C_4H_3O.C_4(H_2Na)O_3 + C_4H_5I = NaI + C_4H_3O.C_4H_2(C_4H_5)O_3.$$
Sodacetic ether. Iodide of ethyl. Ethacetic or butyric ether.

From this ether the ethacetic acid, $HO.C_4H_2(C_4H_5)O_3$, has been prepared and found to be identical with butyric acid, $HO.C_8H_7O_3$.

The connection thus established between butyric acid and the ethyle series helps to explain the production of that acid in the fermentation of sugar.

But butyric ether has also been obtained by another process of substitution, which affords a proof that the same substance may be correctly represented by two distinct rational formulæ.

The substitution of sodium for hydrogen in acetic ether may extend to two atoms of hydrogen, and if the *disodacetic ether* so produced be digested with iodide of methyle, butyric ether is obtained—

$$C_4H_3O.C_4(HNa_2)O_3 + 2C_2H_3I = 2NaI + C_4H_3O.C_4H(C_2H_3)_2O_3.$$
Disodacetic ether. Iodide of methyle. Dimethacetic or butyric ether.

So that butyric acid may be regarded, according to the method by which it is produced, either as ethacetic acid, formed from acetic acid by the substitution of an equivalent of ethyle for one of hydrogen, or as dimethacetic acid, resulting from the substitution of two equivalents of methyle for two of hydrogen.

When disodacetic ether is acted on by iodide of ethyle, it yields diethacetic ether—

$$C_4H_3O.C_4(HNa_2)O_3 + 2C_4H_5I = 2NaI + C_4H_3O.C_4H(C_4H_5)_2O_3.$$
Disodacetic ether. Iodide of ethyle. Diethacetic ether.

* Butyric acid and some of its homologues (as valerianic and caproic) appear to be present in the perspiration of the skin, and to cause the disagreeable odour of close rooms.

This ether has an odour resembling peppermint, and its composition the same as that of caproic ether, $C_4H_5O . C_{12}H_{11}O_3$; but the *diethyl acid* prepared from it, though isomeric with caproic acid ($HO . C_{12}H_{11}$ is not identical with it.

The acid next in the series, œnanthic ($HO . C_{14}H_{13}O_3$), may be obtai from the ether produced by the action of iodide of amyle upon sodac ether—

$$\underset{\text{Sodacetic ether.}}{C_4H_5O . C_4(H_2Na)O_4} + \underset{\substack{\text{Iodide of}\\ \text{amyle.}}}{C_{10}H_{11}I} = NaI + \underset{\text{Amyl-acetic ether.}}{C_4H_5O . C_4H_2(C_{10}H_{11})}$$

From this ether, the amyl-acetic acid, $HO . C_4H_2(C_{10}H_{11})O_3$, which ap to be identical with œnanthic acid, has been obtained.

These reactions help to explain the production of several of the alc corresponding to the acetic series of acids, during the fermentation of g husks (marc of the wine-press).

Among the products of the action of sodium and ethylic iodide upon acetic is a liquid having the composition $C_{16}H_{14}O_6$, which, when distilled with al bases, yields *ethylated acetone*, $C_6H_5(C_4H_5)O_2$, isomeric with the acetone of pr acid (propione, $C_{10}H_{10}O_2$)—

$$C_{16}H_{14}O_6 + 2(BaO . HO) = \underset{\substack{\text{Ethylated}\\ \text{acetone.}}}{C_{10}H_{10}O_2} + \underset{\text{Alcohol.}}{C_4H_6O_2} + 2(BaO . C$$

Another liquid produced by the action of ethylic iodide upon disodacetic e the composition $C_{20}H_{18}O_6$, which furnishes *diethylated acetone*, $C_6H_4(C_4H_5)_2$ distilled with baryta water—

$$C_{20}H_{18}O_6 + 2(BaO . HO) = \underset{\substack{\text{Diethylated}\\ \text{acetone.}}}{C_{14}H_{14}O_2} + \underset{\text{Alcohol.}}{C_4H_6O_2} + 2(BaO .$$

Diethylated acetone is a liquid smelling of camphor, and boiling at 280° isomeric with butyrone, which boils at 290° F., and with œnanthic ald œnanthole, which boils at 312° F.

By treating acetic ether with sodium and methylic iodide, the corre methylated acetones may be obtained.

Methylated acetone, $C_6H_5(C_2H_3)O_2$, has the odour of chloroform, and is with the ethyl-acetyle, $C_4H_3O_2 . C_4H_5$, obtained by the action of zinc-eth chloride of acetyle.

Dimethylated acetone, $C_6H_4(C_2H_3)_2O_2$, has an odour of parsley.

Valerianic acid ($HO . C_{10}H_9O_3$) derives interest from the circu that some of its salts, particularly the valerianate of zinc, are use cinally.

This acid is found in valerian root, and in the berries of the rose. It is one cause of the peculiar odour of decaying cheese whale and seal oils.

Artificially, it is best obtained by distilling fousel oil (amylic $C_{10}H_{12}O_2$) with sulphuric acid and bichromate of potash, when the of the chromic acid converts part of the amylic alcohol into va acid—

$$\underset{\text{Fousel oil.}}{C_{10}H_{12}O_2} + O_4 = \underset{\text{Valerianic acid.}}{C_{10}H_{10}O_4} + 2HO .$$

The distilled liquid is really a mixture of valerianic acid and ate of amyle ($C_{10}H_{11}O . C_{10}H_9O_3$), but when treated with hy

ıe latter is decomposed, yielding fousel oil and valerianate of

$$\underset{\text{nate of amyle.}}{O.C_{10}H_9O_3} + KO.HO = \underset{\text{Fousel oil.}}{C_{10}H_{11}O.HO} + \underset{\text{Valerianate of potash.}}{KO.C_{10}H_9O_3}.$$

tilling the valerianate of potash with sulphuric acid, the valeri- is obtained as an oily liquid of very remarkable odour, which at of butyric acid.

The separation of the volatile acids belonging to the acetic series lem which frequently presents itself to the chemist, and is effected instructive process of *partial saturation*, founded upon the prin- at when a mixture containing two acids with different boiling partially neutralised by an alkali and distilled, the more volatile ro acids (*i.e.*, that having the lower boiling point) will pass over, ıe other remains in combination with the alkali.

plying this method, for example, to a mixture of valerianic acid at 347° F.) and butyric acid (boiling at 315° F.), in unknown ons, the liquid would be divided into two equal parts, one of ould be exactly neutralised with potash, and then distilled to- ith the other half. If there were just enough valerianic acid to with the potash, pure valerianate of potash would be left in the nd the more volatile butyric acid would pass over. If there were lerianic acid than would be required to combine with the potash, ss of that acid would distil over, together with the butyric acid, alerianate of potash alone would be left in the retort. By distill- salt with sulphuric acid, the pure valerianic acid would be ob- and the separation of the rest of the valerianic from the butyric uld be effected by one or two repetitions of the process.

e valerianic acid present in the mixture were not in sufficient to combine with the potash added, then butyrate of potash, as valerianate, would be left in the retort, and pure butyric acid would ver. By distilling the mixture of valerianate and butyrate of with sulphuric acid, a mixture of the two acids would be obtained vould require a repetition of the process.

ıy case, it will be observed that this process must yield one of the a state of purity.

ame principle applies to the separation of three or more volatile ut the process involves, of course, a greater number of distillations.

Soap.—The manufacture of soap affords an excellent instance of ss which was in use for centuries before anything was known of ıciples upon which it is based, for it was not till the researches of ul were published in 1813 that any definite ideas were entertained spect to the composition of the various fats and oils from which e made.

investigations of Chevreul are conspicuous among the labours ıave contributed in so striking a manner to the rapid advancement istry during the present century; undertaken when the chemistry ıic substances had scarcely advanced beyond the dignity of an art, he principles of classification were almost entirely empirical, and any research had been published which could serve as a model, esearches reflect the remarkable sagacity and accuracy of their

The sense of our obligation to this eminent chemist is further in
when we remember that the ultimate analysis of organic substa
then effected by a very difficult and laborious process, whilst the
of combining proportions was so imperfectly understood, that it cou
but little assistance in confirming or interpreting the results of an

All soaps result from the action of the alkalies upon the oils an

In the manufacture of soap, potash and soda are the only alkal
ployed, the former for soft, the latter for hard soaps.

The fatty matters employed by the soap-maker are chiefly tallo
oil, cocoa-nut oil, and kitchen stuff, for hard soaps, and seal oil an
oil for soft soaps.

In the manufacture of hard soap, the alkali is prepared by t
solution of carbonate of soda (soda-ash) with lime to remove the
acid—

$$NaO.CO_2 + CaO.HO = CaO.CO_2 + NaO.H$$

the clear solution of hydrate of soda, or *soda-ley*, being drawn
the insoluble carbonate of lime.

The tallow is at first boiled with a weak soda-ley, because t
which is formed is insoluble in a strong alkaline solution, an
envelope and protect a quantity of undecomposed tallow; in pr
as the saponification proceeds, stronger leys are added, until the
the grease has disappeared. In order to separate the soap
dissolved, advantage is taken of the insolubility of soap in solution
a quantity of common salt being thrown into the boiler, the soa
the surface, when the *spent ley* is drawn off from below, and
transferred to iron moulds that it may harden sufficiently to
into bars.

In order to understand the chemistry of this process, it is nec
know that tallow is a mixture of two fatty substances, one
*stearine** ($C_{114}H_{110}O_{12}$), is solid, and the other, *oleine* ($C_{114}H_{104}O_{1}$
the quantity of stearine being about thrice that of oleine.

When these fats are acted upon by soda, they undergo decom
furnishing stearic and oleic acids, which combine with the soda
soap, whilst a peculiar sweet substance, termed *glycerine*, p
solution; the nature of the decomposition in each case will be u
from the following equations:—

$$\underset{\text{Stearine.}}{C_6H_5O_3.(C_{36}H_{35}O_3)_3} + 3(NaO.HO) = 3(\underset{\text{Stearate of soda.}}{NaO.C_{36}H_{35}O_3}) +$$

$$\underset{\text{Oleine.}}{C_6H_5O_3.(C_{36}H_{33}O_3)_3} + 3(NaO.HO) = 3(\underset{\text{Oleate of soda.}}{NaO.C_{36}H_{33}O_3}) +$$

so that the soap obtained by boiling tallow with soda is a mixt
stearate of soda with about a third of its weight of oleate of
from 20 to 30 per cent. of water.

Palm oil is composed chiefly of *palmitine* ($C_{102}H_{98}O_{12}$), a solid
is resolved by boiling with soda into palmitate of soda (palm oil
glycerine—

$$\underset{\text{Palmitine.}}{C_6H_5O_3.(C_{32}H_{31}O_3)_3} + 3(NaO.HO) = 3(\underset{\text{Palmitate of soda.}}{NaO.C_{32}H_{31}O_3}) +$$

In the fish oils, the predominant constituent is oleine, so t

* Στέαρ, tallow.

hydrate of potash, they yield oleate of potash ($KO.C_{36}H_{33}O_3$), poses the chief part of soft soap.

oap is made from olive oil, which contains oleine and a solid fat *margarine*. The latter appears to be really composed of palmi- earine, so that the Castile soap is a mixture of oleate, palmitate, e of soda.

uliar appearance of mottled soap is caused by the irregular dis- of a compound of the fatty acid with oxide of iron, which self in veins throughout the mass. If the soap contained too r, so as to render it very fluid when transferred to the moulds, compound would settle down to the bottom, leaving the soap hat the mottled appearance is often regarded as an indication oap does not contain an undue proportion of water; it is imi- ever, by stirring into the pasty soap some sulphate of iron and pure ley containing sulphide of sodium, so as to produce the ide of iron by double decomposition.*

manufacture of yellow soap, in addition to tallow and palm oil, able proportion of common rosin (*see* p. 470) is added to the soap fore it is finished.

p is not separated from the water by salt like hard soap, but is l to the required consistency.

rent soaps are obtained by drying hard soap, dissolving it in hot ine, and pouring the strong solution into moulds after the greater e spirit has been distilled off.

d soap is a mixture of soap with silicate of soda.

ne soap is prepared by heating the fat with alkali and a little bout 400° F. for two or three hours, and running the mass at moulds. It is, of course, a mixture of soap and glycerine.

portion of water in soaps is very variable, some specimens contain- en 70 and 80 per cent. The smallest proportion is about 30 per cent. ory of saponification, stated above, has received the strongest ion within the last few years, by the synthetic production of the glycerine and the fatty acids formed in their saponification.

ation of the fatty acids.—All the soaps, when mixed with acids, decomposition, their alkalies combining with the acid added, e fatty acids separate either in the solid form (in the case of stearic itic acids), or as an oily liquid (in the case of oleic acid). Thus, btained by boiling tallow with soda be dissolved in hot water, d with an excess of tartaric acid, an oil rises to the surface which into a buttery mass on cooling. This mass, composed of stearic acids, is submitted to pressure in order to separate the greater ie liquid oleic acid, and the stearic acid which is left is purified llisation, first from alcohol, and afterwards from ether.

acid is thus obtained in transparent colourless plates which have sition $HO.C_{36}H_{35}O_3$; they are, of course, insoluble in water, but n hot alcohol, the solution being acid to test-papers.

e stearates are insoluble in water except those of the alkalies, so solution of common soap (containing stearate of soda) be mixed olution of lime or magnesia, a stearate of lime or magnesia is in the insoluble form, and it will be remembered that this ition of soap is produced by the action of hard waters (page 40).

* which contains much more than 30 per cent. of water is said not to admit of

419. CANDLES.—Since tallow fuses at about 100° F., and [illegible] not below 159°, it is evident that, independently of other [illegible] the latter would be better adapted for the manufacture of candles, [illegible] candles would never soften at the ordinary atmospheric temperature any climate, and would have much less tendency to *gutter* in consequence of the excessive fusion of the fuel around the base of the wick. gases furnished by the destructive distillation of stearic acid in the of the candle burn with a brighter flame than those produced from Accordingly the manufacture of stearine (or more correctly, stearic candles* has now become a very important and instructive branch industry.

The original method of separating the stearic acid from tallow on large scale, consisted in mixing melted tallow with lime and water heating the mixture for some time to 212° by passing steam through The tallow was thus converted into the insoluble stearate and oleate lime, which was drained from the solution containing the glycerine decomposed by sulphuric acid. The mixture of stearic and oleic thus obtained was cast into thin slabs, which were packed between of cocoa-nut matting, and well squeezed in a hydraulic press, which out the oleic acid, leaving the stearic and palmitic acids in a fit st the manufacture of candles.

The separation of the solid fatty acids from tallow and other fa also be effected by the action of sulphuric acid, a process exte applied in this country to palm and cocoa-nut oils. These fats are in copper boilers with about one-sixth of their weight of concentra phuric acid, and heated by steam to about 350° F. for some hours part of the glycerine is converted into sulphoglyceric acid ($C_3H_5O_6$, and the remainder is decomposed by the sulphuric acid, carbonic phurous acids being disengaged, whilst a dark-coloured mixture of stearic, and oleic acids is left. A part of the oleic acid becomes co in this process into *elaidic acid*, which has the same composit differs from oleic acid in fusing at about 113° F., so that the am solid acid obtained by this process is much increased. This mi well washed from the adhering sulphuric and sulphoglyceric ac transferred to a copper still into which a current of steam is passe has been raised to about 600° F. by passing through hot iro These fatty acids could not be distilled alone without decomposi under the influence of a current of steam they pass over readily leaving a black pitchy residue in the retort, which is employed in black sealing wax and for other useful purposes.

The distilled fatty acids are broken up and pressed between c matting to remove the oleic acid.

One great advantage of this process, which is commonly, thou rectly, styled the *saponification by sulphuric acid*, is its allowing version of the worst kinds of refuse fat into a form fit for the mak of candles; thus the fat extracted from bones in the manufactur and that removed from wool in the scouring process, may be t profitable account.

It will be remarked that in this process the palmitic, stearic, acids are formed from the palmitine, stearine, and oleine existi fats, by the assimilation of the elements of water and the su

* *Composite candles* are made of a mixture of stearic and palmitic acids

paration of glycerine, just as in the ordinary process of saponification by eans of alkalies.

Strictly speaking, the action appears to consist of two stages; for when ncentrated sulphuric acid is allowed to act upon the natural fats in the old, it combines with each of their ingredients, forming the acids known s sulphostearic, sulphopalmitic, sulpholeic, and sulphoglyceric, which are oluble in water, though not (with the exception of the last) in water ontaining sulphuric acid.

The second stage consists in the decomposition of the sulpho-fatty acids y the high temperature in contact with steam, the sulphoglyceric acid aving been in great measure decomposed into secondary products before he distillation is commenced.

Within the last few years, the extraction of the solid acids from the atural fats has been effected by a process known as *saponification by team*, which allows the glycerine also to be obtained in a pure state. It s only necessary to subject the fat, in a distillatory apparatus, to the ction of steam, at a temperature of about 600° F., to cause both the atty acids and the glycerine to distil over; the former may be separated as usual into solid and liquid portions by pressure, whilst the glycerine, which is obtained in aqueous solution below the layer of fatty acids, is concentrated by evaporation and sent into commerce as a very sweet colourless viscid liquid. The saponification of palmitine, for instance, by steam, would be represented by the equation—

$$\underset{\text{Palmitine.}}{C_6H_2O_3.(C_{32}H_{31}O_2)_3} + 6HO = 3\underset{\text{Palmitic acid.}}{(HO.C_{32}H_{31}O_2)} + \underset{\text{Glycerine.}}{C_6H_8O_6}.$$

420. In the artificial formation of natural fats, this change has been reversed, for by heating 3 equivalents of stearic, palmitic, or oleic acid with 1 equivalent of glycerine, in a sealed tube, for several hours, to about 500° F., 6 equivalents of water are eliminated, and stearine, palmitine, or oleine is produced.

By a similar process, compounds have been formed from glycerine with one and two equivalents of the fatty acids, so that we are acquainted, in the stearine series, for example, with—

		Stearic acid.	Glycerine.	
Monostearine, .	$C_{42}H_{42}O_8$	$= C_{36}H_{36}O_4$	$+ C_6H_8O_6$	$- 2HO$
Bistearine, . .	$C_{78}H_{76}O_{10}$	$= 2(C_{36}H_{36}O_4)$	$+ C_6H_8O_6$	$- 4HO$
Terstearine . .	$C_{114}H_{110}O_{12}$	$= 3(C_{36}H_{36}O_4)$	$+ C_6H_8O_6$	$- 6HO$

The last representing stearine as it exists in the natural fats.

Nor is it only with the fatty acids, properly so called, that glycerine will furnish *glycerides*, as these bodies are termed, similar compounds having been obtained with acetic and benzoic acids.

The hydrogen-acids are also capable of acting upon glycerine in a similar manner. Thus, when glycerine ($C_6H_8O_6$) is acted on by hydrochloric acid, an oily liquid, *chlorhydrine* ($C_6H_7O_4Cl$), is obtained, the glycerine having combined with 1 equivalent of hydrochloric acid, and 2 equivalents of water having been separated.

Dichlorhydrine ($C_6H_6O_2Cl_2$) results from the union of glycerine with 2 equivalents of hydrochloric acid, and separation of 4 equivalents of water; whilst, to form *trichlorhydrine* ($C_6H_5Cl_3$), 3 equivalents of hydrochloric acid are taken up, and 6 equivalents of water removed.

By the action of oxide of silver, in presence of water, the chlorhydrines may be reconverted into glycerine. The examination of these chlorhydrines has pointed out the method of effecting the conversion of a triatomic alcohol (glycerine) into a

diatomic alcohol (glycol), for if chlorhydrine be acted on by sodium dissolved in cury, in the presence of water, it is converted into the glycol of propylene—

$$\underset{\text{Chlorhydrine.}}{C_6H_7O_4Cl} + HO + Na_2 = \underset{\text{Propyl-glycol.}}{C_6H_8O_4} + NaO + NaCl.$$

This tendency of glycerine to form compounds with the acids formation of which is attended (like that of the ethers from alcohol) separation of the elements of water, has led chemists to look upon rine as an alcohol—a view which is also supported by its combining sulphuric and phosphoric acids to form *sulphoglyceric* ($C_6H_7O_8 . HO$. and *phosphoglyceric* acids, just as alcohol forms sulphovinic and ph vinic acids. A compound has even been obtained, which is believ stand to glycerine in a relation similar to that which ether be alcohol; the formula of this *glyceric ether*, as it is called, is $C_6H_8O_8$ ing from glycerine ($C_6H_8O_6$) by the elements of 3 equivalents of wa

The formation of stearine from stearic acid and glycerine would be quite analogous to that of acetic ether, for example, from aceti and alcohol, as will be seen by comparing the two equations—

$$\underset{\text{Acetic acid.}}{HO . C_4H_3O_3} + \underset{\text{Alcohol.}}{C_4H_5O . HO} = \underset{\text{Acetic ether.}}{C_4H_5O . C_4H_3O_3} + 2H($$

$$\underset{\text{Stearic acid.}}{(3HO . C_{36}H_{35}O_3)} + \underset{\text{Glyceric alcohol (glycerine).}}{C_6H_5O_3 . 3HO} = \underset{\text{Stearine.}}{C_6H_5O_3 . 3C_{36}H_{35}O_3} + 6E$$

The only difference between the two reactions is, that in the latter, 3 valents of acid are concerned, and 3 equivalents of water are rem from the glyceric alcohol. This circumstance, taken together with other features of glycerine, has induced those chemists who con alcohol as formed upon the type of a molecule of water, to look glycerine as derived in a similar manner from 3 molecules of wat which half the hydrogen is replaced by the triatomic radical, *gly* $(\Theta_3H_5)'''$; thus—

Type . . .	$\left.\begin{matrix}H\\H\end{matrix}\right\}\Theta$	Type	$\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}\Theta_3$
Alcohol	$\left.\begin{matrix}\Theta_3H_5\\H\end{matrix}\right\}\Theta$	Glyceric alcohol, or glycerine,	$\left.\begin{matrix}(\Theta_3H_5)'''\\H_3\end{matrix}\right\}\Theta_3$
Ether, .	$\left.\begin{matrix}\Theta_3H_5\\\Theta_3H_5\end{matrix}\right\}\Theta$	Glyceric ether,	$\left.\begin{matrix}(\Theta_3H_5)'''\\(\Theta_3H_5)'''\end{matrix}\right\}\Theta_3$

421. Glycerine is obtained on the small scale by boiling olive oi litharge and water, until the stearic, oleic, and palmitic acids are con into their lead-salts (*lead plaster*), which are insoluble, whilst the rine, together with a little oxide of lead, pass into solution. The precipitated by hydrosulphuric acid, and the filtered liquid concen by evaporation.

The chief uses of glycerine as an application to the skin, and a r in cases of deafness, depend upon its oily consistency, and its w volatility, which preserves surfaces to which it is applied in a moi supple condition.

Glycerine cannot be distilled alone without decomposition, though been seen to be capable of distillation in a current of highly heated When decomposed by distillation, it evolves very irritating vap *acroleine* ($C_6H_4O_2$), which is a constant product of the destructive d tion of fats containing glycerine, and gives rise to the peculiar disa lour of a smouldering tallow candle; composite candles, being v

ric and palmitic acids (without glycerine) do not emit this odour of leine when blown out.

croleine is best obtained in the pure state by distilling glycerine n anhydrous phosphoric acid, which removes 4 equivalents of water $H_6O_3 - 4HO = C_6H_4O_2$). It is a colourless liquid, distinguished by its nsely irritating vapour, which affects the eyes very strongly. From a mical point of view it is interesting, as being the aldehyde of the allyle es (*see* p. 479), and, therefore, another link connecting that series with cerine. By treatment with oxide of silver, acroleine is converted into *ylic acid* ($C_6H_4O_4$), bearing the same relation to acroleine ($C_6H_4O_2$) that tic acid ($C_4H_4O_4$) bears to ordinary aldehyde ($C_4H_4O_2$). The iodide of yle and allylic alcohol have been already noticed (p. 479).

The allyle series, therefore, is perfectly parallel with the ethyle series, d it seems very probable that allylic alcohol is a member of a homo- ous series of alcohols having the general formula $C_{2n}H_{2n}O_2$, with a series acids corresponding to the acetic series, but having the general formula $H_{2n-2}O_4$, of which the following members are known :—

Acrylic Series of Acids.

Acid.	Equivalent Formula.	Source.
Acrylic	$C_6H_4O_4$	Oxidation of acroleine.
Crotonic	$C_8H_6O_4$	Croton-seed oil.
Angelic	$C_{10}H_8O_4$	Angelica root.
Pyroterebic	$C_{12}H_{10}O_4$	Turpentine.
Damaluric	$C_{14}H_{12}O_4$	Cow's urine (βάμαλος, *a calf*).
Campholic	$C_{20}H_{18}O_4$	Camphor.
Moringic	$C_{28}H_{26}O_4$	*Moringa aptera* (oil of ben).
Hypogeic	$C_{32}H_{30}O_4$	Oil of ground nut.
Physetoleic		Sperm-whale oil (*Physeter macrocephalus*).
Oleic	$C_{36}H_{34}O_4$	Most oils.
Doeglic	$C_{38}H_{36}O_4$	Doegling train oil.
Brassic	$C_{44}H_{42}O_4$	Mustard seed (fixed) oil.
Erucic		Colza oil (*Brassica oleifera*).

These acids are monobasic, their salts being formed by the substitution of 1 eq. of metal for 1 eq. of hydrogen, or of 1 eq. of a basic protoxide for 1 eq. of water.

The following table exhibits the principal members of the allyle series, together with the corresponding members of the ethyle series :—

Ethyle Series.		*Allyle Series.*	
Ethyle,	$C_4H_5 . C_4H_5$	Allyle,	$C_6H_5 . C_6H_5$
Ether,	$C_4H_5O . C_4H_5O$	Allylic ether,	$C_6H_5O . C_6H_5O$
Alcohol,	$C_4H_5O . HO$	Allylic alcohol,	$C_6H_5O . HO$
Iodide of ethyle,	C_4H_5I	Iodide of allyle,	C_6H_5I
Acetic ether,	$C_4H_5O . C_4H_3O_3$	Acetate of allyle,	$C_6H_5O . C_4H_3O_3$
Aldehyde,	$C_4H_4O_2$	Allyle aldehyde,	$C_6H_4O_2$ (acroleine)
Acetic acid,	$C_4H_4O_4$	Acrylic acid,	$C_6H_4O_4$
Sulphide of ethyle,	C_4H_5S	Sulphide of allyle,	C_6H_5S (oil of garlic)
Triethylamine,	$N(C_4H_5)_3$	Triallylamine,	$N(C_6H_5)_3$
Hydrated oxide of *Tetrethylium*,	$N(C_4H_5)_4O . HO$	Hydrated oxide of Tetrallylium,	$N(C_6H_5)_4O . HO$

It has been seen (p. 479) that glycerine, when distilled with bromide of phosphorus, yields iodide of allyle (C_6H_5I). When this liquid is treated with bromine it yields a crystallisable *terbromide of allyle*, $C_6H_5Br_3$; and if this be decomposed by acetate of silver, it furnishes the glyceride known as *teracetine*, thus—

$$\underset{\text{Terbromide of allyle.}}{C_6H_5Br_3} + \underset{\text{Acetate of silver.}}{3(AgO.\overline{A})} = \underset{\text{Teracetine.}}{C_6H_5O_3.3\overline{A}} + 3AgBr.$$

When teracetine is submitted to the action of hydrate of baryta, glycerine is reproduced—

$$\underset{\text{Teracetine.}}{C_6H_5O_3.3\overline{A}} + 3(BaO.HO) = \underset{\text{Glycerine.}}{C_6H_8O_6} + \underset{\text{Acetate of baryta.}}{3(BaO.\overline{A})}.$$

This affords an interesting example of the conversion of a monatomic radical, allyle (C_6H_5)′, into a triatomic radical, glyceryle (C_6H_5)″.

422. A very interesting chemical similarity has been pointed out between glycerine and mannite ($C_6H_7O_6$). It will be remembered that the former is a constant product of the alcoholic fermentation, and the latter of a peculiar kind of fermentation (the viscous), to which saccharine liquids are subject.

When mannite is heated, under pressure, with the acids of the acetic series, it forms compounds corresponding to those obtained when glycerine is so treated. Thus, with stearic acid—

$$\underset{\text{Mannite.}}{C_6H_7O_6} + \underset{\text{Stearic acid.}}{3(C_{36}H_{36}O_4)} = \underset{\substack{\text{Terstearomannite,}\\ \text{or mannite stearine.}}}{C_{114}H_{108}O_{11}} + 7HO.$$

But it will be observed that 7 equivalents of water are here eliminated instead of 6 eqs., as in the case of glycerine. The further examination of mannite explains this, for it is not that substance which is the true analogue of glycerine, but one which is obtained by heating mannite to 400° F., when it loses an equivalent of water, and is converted into *mannitane*—

$$\underset{\text{Mannite.}}{C_6H_7O_6} - HO = \underset{\text{Mannitane.}}{C_6H_6O_5}.$$

This mannitane or mannite-glycerine is a viscous substance, presenting a very strong resemblance to glycerine, so that it is not unlikely to have been mistaken for this substance in examining some of the natural fats. The *mannite-glycerides*, or compounds formed by heating mannite with the fatty acids, are scarcely to be distinguished from stearine, palmatine, &c. They are saponified by alkalies in exactly the same manner.

Cane-sugar and grape-sugar are capable of forming compounds corresponding to those obtained by the action of acids upon glycerine and mannite. Thus, if grape-sugar be heated to 250° F. for several hours in contact with stearic acid, it is converted into a fusible solid, insoluble in water, but soluble in alcohol and ether—

$$\underset{\substack{\text{Grape-sugar}\\ \text{(anhydrous).}}}{C_{12}H_{12}O_{12}} + \underset{\text{Stearic acid.}}{2(C_{36}H_{36}O_4)} = \underset{\text{Stearic glucose.}}{C_{84}H_{78}O_{14}} + 6HO.$$

When grape-sugar is heated with tartaric acid, a similar reaction takes place, but the resulting product is a new acid—

$$\underset{\substack{\text{Grape-sugar}\\ \text{(anhydrous).}}}{C_{12}H_{12}O_{12}} + \underset{\text{Tartaric acid.}}{2(2HO.C_8H_4O_{10})} = \underset{\text{Gluco-tartaric acid.}}{2HO.C_{28}H_{16}O_{26}} + 6HO$$

Cane-sugar behaves in a similar manner.

423. *Nitroglycerine*, or *glonoine*.—This violently explosive substance is very easily prepared by dissolving glycerine in a mixture of equal measures the strongest nitric and sulphuric acids, previously cooled, and pouring the solution in a thin stream into a large volume of water, when the nitroglycerine is precipitated as a colourless heavy oil (sp. gr. 1·6). It is advisable to add the glycerine to the mixed acids in very small quantities at a time, and to cool the mixture in a vessel of water after each addition. When the nitroglycerine has subsided, the water may be poured off, and the oil shaken several times with water, so as to wash it thoroughly. The formation of nitroglycerine resembles that of gun-cotton (*see* p. 503), three equivalents of hydrogen being removed from the glycerine by the oxidising action of the nitric acid, and three equivalents of nitric peroxide introduced in their place—

$$\underset{\text{Glycerine.}}{C_6H_8O_6} + 3(HO.NO_5) = \underset{\text{Nitroglycerine.}}{C_6H_5(NO_4)_3O_6} + 6HO.$$

This oil is far more violent in its explosive effects than gun-cotton, more nearly resembling the fulminates, though not so easily exploded. If a drop of nitroglycerine be placed on an anvil and struck sharply, it explodes with a very loud report, even though not free from water; and if a piece of paper moistened with a drop of it be struck, it is blown into small fragments. On the application of a flame or of a red-hot iron to nitroglycerine, it burns quietly; and when heated over a lamp in the open air it explodes but feebly. In a closed vessel, however, it explodes at about 360° F. with great violence. For blasting rocks the nitroglycerine is poured into a hole in the rock, and exploded by the concussion caused by a particular kind of fuze charged with a little gunpowder. It has been stated to produce the same effect in blasting as ten times its weight of gunpowder, and much damage has occurred from the accidental explosion of nitroglycerine in course of transport. When nitroglycerine is kept, especially if it be not thoroughly washed, it decomposes, with evolution of nitrous fumes and formation of crystals of oxalic acid; and it may be readily imagined that, should the accumulation of gaseous products of decomposition burst one of the bottles in a case of nitroglycerine, the concussion would explode the whole quantity.

Nitroglycerine is readily soluble in ether and in wood-spirit, and somewhat less soluble in alcohol; it is reprecipitated by water from these last solutions. It solidifies at 40° F. A drop of nitroglycerine is said to cause very violent headache, and in larger doses it appears to be decidedly poisonous.

Oils and Fats.

424. A very remarkable feature in the history of the fats is the close resemblance in chemical composition and properties which exists between them, whether derived from the vegetable or the animal kingdom. They all contain two or more neutral substances which furnish glycerine when saponified, together with some of the acids of the acetic series or of series closely allied to it.

One of the most useful vegetable fatty matters is *palm-oil*, which is extracted by boiling water from the crushed fruit of the *Elais Guineensis*, an African palm. It is a semi-solid fat, which becomes more solid when kept, since it then undergoes a species of fermentation, excited apparently

by an albuminous substance contained in it, in consequence of which the palmitine ($C_{102}H_{98}O_{12}$) is converted into glycerine and palmitic acid. The bleaching of palm-oil is effected by the action of a mixture of sulphuric acid and bichromate of potash, which oxidises the yellow colouring matter.

Cocoa-nut oil is also semi-solid, and is remarkable for the number of acids of the acetic series which it yields when saponified, viz., capric, caprylic, rutic, lauric, myristic, and palmitic.

These fats are chiefly used in the manufacture of soap and candles.

Salad oil, or *sweet oil* (olive oil), is obtained by crushing olives, and an inferior kind which is used for soap is obtained by boiling the crushed fruit with water. When exposed to a temperature of about 32° F. a considerable portion of the oil solidifies; this solid portion is generally called *margarine* ($C_{108}H_{104}O_{12}$); it is much less soluble in alcohol than stearine, though more so than palmitine. When saponified, margarine yields glycerine and *margaric acid* ($C_{34}H_{34}O_4$). This acid appears to be really composed of stearic and palmitic acids, into which it may be separated by repeated crystallisation from alcohol, when the palmitic acid is left in solution. The fusing-point of margaric acid is 140° F., that of stearic being 159°, and that of palmitic, 144°, but a mixture of 10 parts of palmitic with 1 part of stearic acid fuses at 140°.

That portion of the olive oil which remains liquid below 32° consists of *oleine* ($C_{114}H_{104}O_{12}$), and forms nearly three-fourths of its weight. Oleine is not so easily saponified as the solid fats, and is resolved by that process into glycerine and oleic acid ($C_{36}H_{34}O_4$), which differs from the other fatty acids by remaining liquid at temperatures above 40° F., and by absorbing oxygen from the air, when it is converted into a new acid which is not solidified by cold.

Oleic acid is used in greasing wool for spinning, being much more easily removed by alkalies than olive oil which was formerly employed. Oleate of ammonia is sometimes employed as a mordant for the aniline dyes on cotton.

The characteristic feature of oleic acid is its furnishing a solid crystallised acid when submitted to destructive distillation; this acid is called *sebacic acid*, and is one of a series of bibasic acids, most of the other members of which may be obtained from oleic acid by the action of nitric acid.

Bibasic Fatty Acid Series.

Acid.	Equivalent Formula.	Source.
Oxalic .	$C_4H_2O_8$	*Oxalis acetosella* (wood sorrel), &c.
Malonic .	$C_6H_4O_8$	Oxidation of malic acid.
Succinic .	$C_8H_6O_8$	Amber (*succinum*).
Lipic .	$C_{10}H_8O_8$	Oxidation of oleic acid (λίπος, *fat*).
Adipic .	$C_{12}H_{10}O_8$	,, ,, (*adeps*, *fat*).
Pimelic .	$C_{14}H_{12}O_8$	,, ,, (πῖμελή, *fat*).
Suberic .	$C_{16}H_{14}O_8$	Oxidation of stearic acid, and of cork (*suber*).
Anchoic * .	$C_{18}H_{16}O_8$	Oxidation of Chinese wax, and of cocoa-nut oil.
Lepargylic † .		
Sebacic .	$C_{20}H_{18}O_8$	Distillation of oleic acid.

* From ἀγχω, to throttle, from its suffocating vapours.
† From λεπαργος, having white skin.

tral salts of the acids of this series are formed by the displace-
o equivalents of hydrogen by a metal, or of two equivalents of
a basic protoxide. Thus, neutral succinate of potash has the
n $C_8(H_4K_2)O_8$, or $2KO . C_8H_4O_6$.

orthy of remark, that nine acids of the series, $C_{2n}H_{2n}O_4$ (from
apric inclusive), are found among the products of the action of
upon oleic acid.

ll known that salad oil becomes rancid, and exhales a disagree-
after being kept for some time. This appears to be due to a
on similar to that noticed in the case of palm oil, originally
the action of atmospheric oxygen upon albuminous matters
the oil; the neutral fatty matters are thus partly decomposed,
ification, their corresponding acids being liberated, and giving
case of the higher members of the acetic series, such as caproic
anic) to the disagreeable odour of rancid oil. By boiling the
with water, and afterwards washing it with a weak solution of
y be rendered sweet again.

oil, extracted by a process similar to that employed for olive oil,
similar in composition; but *colza oil*, obtained from the seeds
ssica oleifera, contains only half its weight of oleine, and hence
more readily than the others.

l is largely used for burning in lamps, and undergoes a process
ion from the mucilaginous substances, which are extracted with
seed, and leave a bulky carbonaceous residue when subjected
ive distillation in the wick of the lamp. To remove these the
ated with about 2 per cent. of oil of vitriol, which carbonises
ginous substances, but leaves the oil untouched. When the
us flocks have subsided, the oil is drawn off, washed to remove
nd filtered through charcoal.

oil, obtained from the seeds of the flax plant, is much richer in
a any of the foregoing, exhibiting no solidification till cooled
0° F. below the freezing point. It exhibits, however, in a far
ree, a tendency to become solid when exposed to the air, which
ed for it the name of a *drying oil*, and renders it of the greatest
ters. This solidification is attended with absorption of oxygen,
s place so rapidly in the case of linseed oil, that spontaneous
a has been known to take place in masses of rag or tow which
smeared with it.*

lency of linseed oil to solidify by exposure is much increased by
with about $\frac{1}{20}$th of litharge, or $\frac{1}{70}$th of binoxide of manganese;
es are technically known as *dryers*, and oil so treated is called
ed oil. The action of these metallic oxides is not well understood.
ng drying tendency of linseed oil is supposed to be due to a
in the oleine, which is said not to be ordinary oleine, but to
ifferent acid, *linoleic acid*, when saponified. When linseed oil
for some time to a high temperature, it becomes viscous and
l is used in this state for the preparation of printing-ink. If
oil be boiled with dilute nitric acid, it is converted into *artifi-*
houc, which is used in the manufacture of surgical instruments.
rty appears to be connected with the drying qualities of the oil.

the oxidation, a volatile compound is formed which resembles acroleine in
lours unsized paper brown. It has been suggested that the brown colour
ell of old books may be due to the oxidation of the oil in the printing-ink.

Castor oil, obtained from the seeds of *Ricinus communis*, also yield... peculiar acid when saponified, termed *ricinoleic* ($HO . C_{36}H_{34}O_5$), ... taining two more equivalents of oxygen than oleic acid, which it ... resembles. The destructive distillation of castor oil yields ... *acid* ($HO . C_{14}H_{13}O_3$), and *œnanthole* or *œnanthic aldehyde* ($C_{14}H_{14}O_2$) ... by distilling it with hydrate of potash, caprylic alcohol ($C_{16}H_{18}O_2$) is ... tained. As in the case of olive oil, the *cold drawn* castor oil, which ... expressed from the seeds without the aid of heat, is much less liable ... become rancid. Castor oil is much more soluble in alcohol than ... other of the fixed oils.

The various *fish oils*, such as seal and whale oil, also consist chiefly ... oleine, and appear to owe their disagreeable odour to the presence of ... tain volatile acids, such as valerianic.

Cod-liver oil appears to contain, in addition to oleine and stearine, ... small quantity of *acetine* ($C_{18}H_{14}O_{12}$), which yields acetic acid and glycerine ... when saponified. Some of the constituents of bile have also been found ... in it, as well as minute quantities of iodine and bromine.

Butter contains about two-thirds of its weight of solid fat, which consists in great part of margarine (*see* p. 580), but contains also *butine*, which yields glycerine and *butic acid* ($HO . C_{40}H_{39}O_2$) when saponified. The liquid portion consists chiefly of oleine. Butter also contains small quantities of butyrine, caproine, and caprine, which yield, when saponified, glycerine and butyric ($HO . C_8H_7O_3$), caproic ($HO . C_{12}H_{11}O_3$), and caprine ($HO . C_{20}H_{19}O_3$) acids, distinguished for their disagreeable odour.

Fresh butter has very little odour, being free from these volatile acids, but if kept for some time, especially if the caseine of the milk has been imperfectly separated in its preparation, spontaneous resolution of the fats into glycerine and the volatile disagreeable acids takes place. By salting the butter this change is in great measure prevented.

The fat of the sheep and ox (*suet*, or when melted, *tallow*) consists chiefly of stearine, whilst in that of the pig (*lard*) oleine predominates to ... the same extent as in butter. Margarine (or palmitine ?) is also present in these fats.

Human fat contains chiefly oleine and margarine (or, if we do not admit the independent existence of the latter, palmitine and stearine).

Sperm oil, which is expressed from the spermaceti found in the head of the sperm whale, owes its peculiar odour to the presence of a fat which has been called *phocenine*, but which appears to be *valerine*, as it yields glycerine and valerianic acid ($HO . C_{10}H_9O_3$) when saponified.

The beautiful solid crystalline fat, known as *spermaceti* or *cetine*, differs widely from the ordinary fatty matters, for when saponified (which is easily effected), it yields no glycerine, but in its stead another alcohol termed *ethal* ($C_{32}H_{34}O_2$), which is a white crystalline solid, capable of being distilled without decomposition.

The soap prepared from spermaceti, when decomposed by an acid, yields palmitic acid ($HO . C_{32}H_{31}O_3$), (formerly called *ethalic acid*), to which ethal is the corresponding alcohol.

Palmitic acid and ethal are formed from spermaceti by the assimilation of the elements of water, just as stearic acid and glycerine are formed from stearine.

$$\underset{\text{Spermaceti, or cetine.}}{C_{64}H_{64}O_4} + 2HO = \underset{\text{Ethal.}}{C_{32}H_{34}O_2} + \underset{\text{Palmitic acid.}}{HO . C_{32}H_{31}O_3} .$$

Upon the compound radical theory, ethal would be represented as the hydrated oxide of *cetyle* ($C_{32}H_{33}$)O . HO, and as the alcohol of the cetyle series running parallel with the ethyle series. The following characteristic members of the series have been studied :—

Cetyle Series.		*Ethyle Series.*	
Cetylene,	$C_{32}H_{32}$	Ethylene,	C_4H_4
Cetylic ether,	$C_{32}H_{33} . O$	Ether,	C_4H_5O
Ethal,	$C_{32}H_{33}O . HO$	Alcohol,	$C_4H_5O . HO$
Palmitic acid,	$C_{32}H_{31}O_3 . HO$	Acetic acid,	$C_4H_3O_3 . HO$
Spermaceti,	$C_{32}H_{33}O . C_{32}H_{31}O_3$	Acetic ether,	$C_4H_5O . C_4H_3O_3$

Chinese wax, the produce of an insect of the cochineal tribe, is analogous in its chemical constitution to spermaceti. When saponified by fusion with hydrate of potash, it yields *cerotine* or *cerylic alcohol* ($C_{54}H_{55}O . HO$), corresponding to ethal, and *cerotic acid* ($HO . C_{54}H_{53}O_3$), corresponding to palmitic acid. Cerotic acid is also contained in ordinary bees' wax, from which it may be extracted by boiling alcohol, and crystallises as the solution cools. It forms about two-thirds of the weight of the wax.

Bees' wax also contains about one-third of its weight of *myricine* ($C_{60}H_{62}O_4$), a substance analogous to spermaceti, which yields, when saponified, palmitic acid and *melissine* ($C_{60}H_{61}O . HO$), an alcohol corresponding to ethal. The colour, odour, and tenacity of bees' wax appear to be due to the presence of a greasy substance called *cerolcine*, which forms about one-tenth of the wax, and has not been fully examined. The *tree-wax* of Japan is said to be pure palmitine.

Wax is bleached for the manufacture of candles, by exposing it in thin strips or ribands to the oxidising action of the atmosphere, or by boiling it with nitrate of soda and sulphuric acid. Chlorine also bleaches it, but displaces a portion of the hydrogen in the wax, taking its place and causing the evolution of hydrochloric acid vapours when the wax is burnt.

The following table includes the principal fatty bodies and their corresponding acids, with their fusing points :—

Neutral Fats.	Equivalent Formula.	Chief Source.	Fusing Point.	Fatty Acids.	Equivalent Formula.	Fusing Point.
Stearine*	$C_{114}H_{110}O_{12}$	Tallow	125° to 157°	Stearic	$C_{36}H_{36}O_4$	159°
Palmitine	$C_{102}H_{98}O_{12}$	Palm oil	114° to 145°	Palmitic	$C_{32}H_{32}O_4$	144°
Margarine	$C_{106}H_{104}O_{12}$	Olive oil	116°	Margaric	$C_{34}H_{34}O_4$	140°
Oleine	$C_{114}H_{104}O_{12}$	,,	Below 32°	Oleic	$C_{36}H_{34}O_4$	40°
Cetine	$C_{64}H_{64}O_4$	Spermaceti	120°	Palmitic	$C_{32}H_{32}O_4$	144°
Myricine	$C_{62}H_{62}O_4$	Bees' wax	162°	,,		

VEGETABLE ACIDS.

425. *Oxalic acid.*—This very poisonous acid occurs pretty abundantly in the vegetable kingdom, being found in the leaves of the wood sorrel as binoxalate of potash (*salt of sorrel*, $KO . HO . 2C_2O_3 + 2Aq.$), in the stalks of rhubarb, in some sea-weeds, as oxalate of soda, and in lichens, some of which contain more than half their weight of oxalate of lime. Oxalate of lime has also been found in wood. In certain unhealthy conditions of the

* Stearine and palmitine are said to present three modifications with different fusing points.

animal frame, oxalate of lime is produced, being either excreted in urine, or forming a calculus (*mulberry calculus*) in the bladder. In cases the oxalic acid appears to be formed in consequence of an imp tion in that oxidising process by which the carbon and hydrogen various parts of the frame are finally converted into carbonic acid and water (HO), the production of oxalic acid (C_2HO_3) represents penultimate stage of that process.

With the exception of carbonic acid, no carbon compound is more monly met with than oxalic acid, as a product of the action of oxi agents upon organic substances, especially upon those which do not tain nitrogen, such as sugar ($C_{12}H_{11}O_{11}$), starch ($C_{12}H_{10}O_{10}$), and fibre.

Oxalic acid is largely employed in calico-printing, in cleansing and brass, as a solvent for Prussian blue in the preparation of bl &c., and for taking iron-mould out of linen. It is manufactured large scale by oxidising saw-dust with a mixture of hydrate of pota hydrate of soda; the latter would not produce oxalic acid with hydrate of potash, and this alone would be too expensive. 1 eq. of of potash and 2 eqs. of hydrate of soda are mixed in solution, which have the sp. gr. 1·35, made into a thick paste with sawdust, and upon iron plates for several hours; hydrogen is evolved, from the position of the water in the alkaline hydrates, the oxygen se convert the wood into oxalic acid, which forms more than one-f the weight of the grey mass finally obtained. On treating this m cold water, a quantity of oxalate of soda is left undissolved; this with hydrate of lime, when the oxalic acid is converted into the oxalate of lime, and hydrate of soda is dissolved; the oxalate then decomposed by dilute sulphuric acid, when the sparingl sulphate of lime is formed, and the solution yields crystals of o ($HO.C_2O_3.2Aq.$) on evaporation. The whole of the alkali employed is recovered by evaporating the liquors to dryness, ca destroy organic matter, and decomposing the alkaline carbon hydrate of lime. The sawdust yields about half its weight of c oxalic acid.

Before the introduction of this process, oxalic acid was sold twice its present cost, being then usually obtained by the actio acid either upon molasses or upon starch-sugar* (p. 495) vessels, which were found to remain unattacked by the acid as lo sugar remained unoxidised.

For experiment on the small scale, oxalic acid may be prepared by gen 100 grains of starch with 1¼ measured ounce of nitric acid (sp. gr. abundant fumes of nitrous acid (NO_3) will indicate the deoxidation suff nitric acid. When this has abated, the solution may be transferred to slowly evaporated to about one-sixth of its bulk; on cooling, a mass o four-sided prismatic crystals of oxalic acid will be obtained.

The crystals of oxalic acid may be represented by the empiric $C_2H_3O_4$, but when they are heated to 212° F. they lose wate first, if the heat be suddenly applied,† but effloresce without heated gradually. The dried or effloresced oxalic acid has the tion C_2HO_3, showing that 2 eqs. of water of crystallisation have

* Hence the common name, *acid of sugar*.

† By suddenly heating the crystals with a lamp in a test-tube, much of the dimed in long prismatic crystals.

d that the crystals would be more correctly represented by
aq. On neutralising oxalic acid with potash and soda, salts are
hich, when dried at 212° F., have the composition $KO.C_2O_3$,
C_2O_3, and if solutions of these salts be precipitated by nitrate
of silver, the oxalates of lead ($PbO.C_2O_3$) and of silver
$_3$) are obtained. Hence it would appear that the composition
ous oxalic acid is C_2O_3, and that the acid dried at 212° F.
represented as $HO.C_2O_3$. All attempts, however, to procure
have failed. If the dried acid be heated to about 320° F., it
n crystals, but above that temperature it is decomposed into
onic acid, carbonic oxide, and some formic acid (*see* p. 567).
ted with dehydrating agents, such as sulphuric acid, it is also
d into carbonic acid and carbonic oxide (p. 79). It would
erefore, more consistent with the results of experiment, not to
n the existence of the C_2O_3, but to write the dried oxalic acid
representing its salts as being formed by the displacement of
gen by a metal, thus, oxalate of potassium, C_2KO_4, oxalate of
gO_4. But oxalic acid has the power of forming acid salts, in
ly a part of the hydrogen is displaced by the metal, such as
of potassium, $KO.HO.2C_2O_3$, or $C_4(KH)O_8$; it also forms two
ethers, *oxalic ether* or oxalate of ethyle, $C_4H_5O.C_2O_3$, or
$_4$, and binoxalate of ethyle or *oxalovinic acid*, $C_4H_5O.HO.2C_2O_3$,
$_3)HO_8$; so that it would appear to be necessary that oxalic acid
represented by the formula $C_4H_2O_8$, when it would be a *bibasic*
iring 2 eqs. of a metal to form a neutral salt. It will be seen
ormula has been adopted at p. 580, where oxalic acid is repre-
the first member of the bibasic fatty acid series.

acid is rather sparingly soluble in cold water, requiring about
its weight; hot water dissolves it more abundantly, and it is
y soluble in alcohol. The aqueous solution is intensely acid,
ly resembling the strong mineral acids than one of vegetable
d is exceedingly poisonous, a property which is the more dan-
account of the resemblance of the crystallised oxalic acid to
lts (sulphate of magnesia), from which, however, it may be
tinguished by its sour taste and by the action of heat, which
lissipates the oxalic acid, but only expels water from Epsom
rtunately, a considerable quantity of the acid is required to
th, in ordinary cases 100 grains or more. The chemical anti-
loyed to counteract its effect is chalk suspended in water, the
he chalk combining with the acid to form the insoluble and
oxalate of lime ($CaO.C_2O_3$). The insolubility of the oxalate of
ers the oxalic acid one of the most delicate tests for lime, which
tected, for example, in common water, by adding oxalic acid
ht excess of ammonia, when a white cloud of oxalate of lime is

Conversely, of course, salts containing calcium (chloride of
or instance) may be employed to detect oxalic acid, the precipi-
ate of lime being distinguished from other similar precipitates by
ility in acetic acid.

ght be expected from its composition (C_2HO_4), oxalic acid is
verted into carbonic acid and water by oxidising agents; thus,
solution of oxalic acid be poured upon powdered binoxide of
e, violent effervescence takes place from the rapid evolution of
cid.

Binoxalate of potash ($KO.HO.2C_2O_3 + 2Aq.$, or KHC_2O_4) sold under the names of *salt of sorrel* and *essential salt of* employed for the same purposes as oxalic acid. It is a salt, requiring 40 parts of cold water to dissolve it, and caused accidents by being mistaken for cream of tartar potash), from which it is readily distinguished by the which chars the bitartrate, but not the binoxalate, an taining carbonate of potash being left in both cases.

Quadroxalate of potash ($KO.3HO.4C_2O_3 + 4Aq.$, or KHC_2O_4 is also sometimes sold as salts of lemon; it is even less binoxalate.

Oxalate of ammonia ($NH_3.HO.C_2O_3 + Aq.$, or $(NH_4)C_2O_4$ much used in chemical analysis as a precipitant for lime, is mixing solution of oxalic acid with a slight excess of ammonia, porating the solution, from which the oxalate of ammonia cooling, in fine prismatic needles.

The action of heat upon this salt has been described at p. 542.

Oxalate of silver ($AgO.C_2O_3$, or $Ag_2C_2O_4$) is obtained as a white pitate when nitrate of silver is added to oxalate of ammonia. markable for being decomposed with a slight explosion when the dry state, metallic silver being left, $AgO.C_2O_3 = Ag + 2O_2$.

426. *Tartaric acid.*—The most important of the vegetable acids is taric acid ($C_8H_6O_{12}$), which occurs in many fruits, but more especially the grape, the juice of which deposits it, during fermentation, in the of bitartrate of potash, which is known in commerce as *tartar* or This salt dissolves with difficulty in cold water, but may be dissolved boiling water, from which it crystallises in prisms on cooling. thus purified, it is known as *cream of tartar*, and has the composition $KO.C_8H_5O_{11}$, representing tartaric acid in which the elements of equivalent of water have been replaced by those of potash. The solution of this salt is acid to test-papers, and if it be neutralised with potash evaporated, it yields crystals of a very soluble salt, having the composition $2KO.C_8H_4O_{10}$. This is regarded as the neutral tartrate of potash, of tartar being a bitartrate, $KO.HO.C_8H_4O_{10}$, inasmuch as tartaric is a bibasic acid, requiring two equivalents of an alkali to form a salt. The crystallised tartaric acid is therefore regarded as $2HO.C$ the two equivalents of water being replaced by an alkali in order a neutral salt, whilst, if half the water only be replaced, an acid bitartrate is produced.

In order to prepare tartaric acid, which is largely used in dyeing calico-printing, the impure bitartrate of potash is boiled with water carbonate of lime (chalk) is added as long as it causes effervescence the escape of carbonic acid; the result of this change is the formation tartrate of lime, which is insoluble, and tartrate of potash, which in the water—

$$\underset{\text{Bitartrate of potash.}}{2(KO.HO.C_8H_4O_{10})} + \underset{\text{Carbonate of lime.}}{2(CaO.CO_2)} =$$

$$\underset{\text{Tartrate of potash.}}{2KO.C_8H_4O_{10}} + \underset{\text{Tartrate of lime.}}{2CaO.C_8H_4O_{10}} + 2HO + 2CO_2$$

Chloride of calcium is then added to the mixture, which converts whole of the tartaric acid into the insoluble tartrate of lime—

$$2KO.C_8H_4O_{10} + 2CaCl = 2KCl + 2CaO.C_8H_4O_{10}.$$

...te of lime is strained off, washed, and boiled with diluted sul-...id, when sulphate of lime remains undissolved, and tartaric acid ...btained in crystals by evaporating the filtered solution—

$$\underset{\text{...e of lime.}}{C_8H_4O_{10}} + 2(HO.SO_3) = \underset{\text{Tartaric acid.}}{2HO.C_8H_4O_{10}} + 2(CaO.SO_3).$$

...ansparent prisms are thus obtained, which are very soluble in ...When kept, the solution, unless very strong, deposits a curious ...growth, and acetic acid is found in it. When heated to about ... the crystals fuse without loss of weight; but on examining the ...ass, it is found to be no longer tartaric acid, but a mixture of two ...ds. One of these, *metatartaric acid*, has the same formula as tar-...id ($2HO.C_8H_4O_{10}$), but cannot be crystallised. Its salts are more ... in water than the tartrates, and are converted into the latter when ...with water. The other acid, *isotartaric*, is also uncrystallisable, ...s the formula ($HO.C_8H_5O_{11}$), being a monobasic acid, one equiva-...f the basic water of the tartaric acid having been incorporated with ...id itself. The isotartrate of potash ($KO.C_8H_5O_{11}$) has the same ...osition as the bitartrate ($KO.HO.C_8H_4O_{10}$), but is far more soluble. ...converted into that salt by boiling with water.

... 374° F. tartaric acid loses its basic water, and is converted into *tar-...anhydride* ($C_8H_4O_{10}$), which is a white insoluble substance, convertible ...tartaric acid by prolonged contact with water.

...rtar-emetic.—One of the commonest salts of tartaric acid is *tartar-...ic*, the double tartrate of antimony and potash, which is prepared by ...ing antimony with sulphuric acid, driving off the excess of acid by ..., and digesting the residual teroxide of antimony with cream of tartar ... a little water for some hours. The changes involved in the process ...thus represented—

$$Sb_2 + 3(HO.SO_3) = 2SbO_3 + 3HO + 3SO_3$$

$$\underset{\text{Bitartrate of potash.}}{SbO_3 + KO.HO.C_8H_4O_{10}} = \underset{\text{Tartar-emetic.}}{KO.SbO_3.C_8H_4O_{10}} + HO.$$

...n boiling the mixture with water, and filtering, the cooled solution ...posits octahedral crystals, of the formula $KO.SbO_3.C_8H_4O_{10}.Aq$.

The water of crystallisation may be expelled at 212° F.; and if the salt be ...eated to 400° F. it loses two additional equivalents of water, and becomes $KO.SbO_3.C_8H_2O_8$, which is reconverted into tartar-emetic when dissolved ...n water.

When a little hydrochloric acid is added to a solution of tartar-emetic, a precipitate of teroxide of antimony is formed, which dissolves easily in an excess of the acid. If kept for a length of time in solution, tartar-emetic is decomposed, octahedral crystals of teroxide of antimony being deposited, and the solution ceases to be precipitated by hydrochloric acid. The reaction to test-paper, which was slightly acid, is now slightly alkaline.

Compounds perfectly analogous to tartar-emetic have been obtained, in which the antimony is replaced by boron or by arsenic, and the potassium by silver, lead, or sodium.

It will be observed that tartar-emetic, and its analogues, present an anomaly in their composition, for it might be expected that the teroxide of antimony (SbO_3) would replace three equivalents of potash instead of one. The composition of the substance $KO.SbO_3.C_8H_2O_8$ is very singular, *but it might be reconciled* with that of crystallised tartaric acid by repre

senting it thus, $C_8(H_2KSb'')O_{12}$, that is, crystallised tartaric acid ($C_8H_6O_{12}$) in which one equivalent of hydrogen has been replaced by potassium, and three equivalents by the triatomic antimony.

The beautiful prismatic crystals known as *Rochelle salt* consist of double tartrate of potash and soda ($KO.NaO.C_8H_4O_{12}$, 8Aq.), prepared by neutralising cream of tartar with carbonate of soda.

Tartaric acid has been obtained artificially by the action of nitric acid upon sugar of milk or gum, which supplies a link of connection between this acid and the members of the sugar group which accompany it in plants.

Tartaric acid is easily convertible into succinic and malic acids, as might be anticipated from an inspection of their formulæ—

Tartaric acid, . .	$2HO.C_8H_4O_{12}$
Malic „ . .	$2HO.C_8H_4O_8$
Succinic „ . .	$2HO.C_8H_4O_6$

When tartaric acid is heated with phosphorus and iodine in the presence of water (or, which amounts to the same thing, when it is heated with hydriodic acid), the acid is deoxidised, and malic and succinic acids are produced, thus—

$$\underset{\text{Tartaric acid.}}{2HO.C_8H_4O_{10}} + 4HI = \underset{\text{Succinic acid.}}{2HO.C_8H_4O_6} + I_4 + 4HO.$$

Tartaric and malic acids are frequently associated in fruits, and succinic acid is found among the products of fermentation of grape-juice.

Succinic acid may be reconverted into tartaric acid by heating it with bromine and water, when it is converted into bibromosuccinic acid, $2HO.C_8(H_2Br_2)O_6$, which furnishes tartaric acid when decomposed with oxide of silver—

$$\underset{\text{Bibromosuccinic acid.}}{2HO.C_8(H_2Br_2)O_6} + 2AgO + 2HO = \underset{\text{Tartaric acid.}}{2HO.C_8H_4O_{10}} + 2AgBr.$$

When bromosuccinic acid, $2HO.C_8(H_2Br)O_6$, is decomposed with oxide of silver, malic acid is formed—

$$\underset{\text{Bromosuccinic acid.}}{2HO.C_8(H_2Br)O_6} + 3AgO = \underset{\text{Malate of silver.}}{2AgO.C_8H_4O_6} + AgBr + HO.$$

427. The tartaric acid found in grapes is accompanied, particularly in those of certain vintages and districts, by another acid called *racemic* or *paratartaric* acid, which has the same composition as tartaric acid, but crystallises with two equivalents of water ($2HO.C_8H_4O_{10}.2Aq.$) The crystalline forms of these acids are the same, but the crystals of racemic acid effloresce, from loss of water, when exposed to the air. Solution of racemic acid is precipitated by the salts of lime, which do not precipitate tartaric acid unless it be previously neutralised. Moreover, although racemic acid forms, with potash and oxide of antimony, a salt corresponding in composition to tartar-emetic, this does not crystallise in octahedra, but in tufts of needles.

There is a marked difference in the action of these two acids and their salts upon polarised light, for solutions of racemic acid and the racemates do not alter the plane of polarisation, whilst tartaric acid and the tartrates rotate it to the right.

On carefully examining the crystalline forms of the tartrates, Pasteur observed that they generally presented an exception to that law of crystalline symmetry, which requires that a modification existing on any edge or face of a crystal should be repeated on all its other similar edges or faces, whereas in the crystals of the tartrates, certain of the edges are truncated without any corresponding modification of the others, and *hemihedral* forms are thus produced. Now, in general, it is found that if a substance forms hemihedral crystals, their hemihedrism is of such a character that they can be superposed upon each other, so that the united crystals shall exhibit

perfect symmetry upon each side of the plane of junction; but the hemihedrism of the tartrates is such, that the crystals do not exhibit this symmetry when superposed upon each other, but when one is superposed upon the reflection of the other in a mirror, so that instead of presenting crystals which are, as usual, partly right and partly left-handed in their want of symmetry, the crystals of the tartrates are either all right-handed or all left-handed hemihedral crystals.

When the action of solutions of these salts upon polarised light came to be examined, it was found that the right-handed crystals always rotated the plane of polarisation to the right, whilst the left-handed crystals produced a left-handed rotation.

On separating the acids from these salts, they resembled each other precisely in all their chemical properties, but the acid from the right-handed salts furnished crystals which were hemihedral right-handedly, whilst that of the left-handed salts furnished left-handed hemihedral crystals; moreover, the solution of the right-handed acid exerted a right-handed rotation upon the plane of polarisation, which was turned in the opposite direction by a solution of the left-handed acid.

The former acid has been named dextro-tartaric acid, and is the usual form in which this acid is met with; the other acid has been called lævo-tartaric acid. In their chemical relations these acids are perfectly identical; for the chemist they are both the same tartaric acid, equally well adapted for all the uses to which this acid is applied.

Pasteur found that the double racemate of soda and ammonia furnished a crop of crystals containing both right-handed and left-handed hemihedral forms, and on separating them by hand, he found that the action of their solutions on polarised light corresponded with their hemihedrism, and on isolating the acids, the right-handed crystals furnished dextro-tartaric, the left-handed, lævo-tartaric acid.

This analysis of racemic acid was soon confirmed by its synthesis. On mixing concentrated solutions of equal parts of dextro-tartaric and lævo-tartaric acids, a considerable rise of temperature was observed, showing that combination had taken place, and the solution which had no longer the power of rotating the plane of polarisation furnished crystals of racemic acid.

This remarkable instance of chemical combination between two acids which are, in their chemical properties, perfectly identical, to furnish a new acid differing from both, affords, by analogy, some support to the theory of the *duplex* constitution of many elementary and compound bodies.

428. *Citric acid* ($C_{12}H_8O_{14}$) occurs in lemons, oranges, and most acidulous fruits. It is prepared from lemon-juice, which contains the acid in a free state, by neutralising it with chalk, when the citrate of lime ($3CaO . C_{12}H_5O_{11}$) is obtained, which is decomposed by dilute sulphuric acid; the filtered solution, when evaporated, yields prismatic crystals of citric acid, which contain $C_{12}H_8O_{14} . 2Aq$. They fuse at 212°F., and lose the two equivalents of water of crystallisation. From the formula of the citrate of lime, it will be seen that citric acid is tribasic, and should be written $3HO . C_{12}H_5O_{11}$; hence, like ordinary phosphoric acid, it forms three series of salts. The citrates of soda, for example, have the composition—

$$3NaO . C_{12}H_5O_{11} . 11Aq.$$
$$NaO . 2HO . C_{12}H_5O_{11} . 2Aq.$$
$$2NaO . HO . C_{12}H_5O_{11} . 2Aq.$$

When citric acid is heated above 300° F., it is converted into *aconitic acid* ($3HO . C_{12}H_3O_9$), another vegetable acid found in the different varieties of monkshood (*aconitum*).

Citric acid is employed in dyeing and calico-printing, as well as in medicine.

By fermentation in contact with yeast, the citrate of lime is converted into acetate and butyrate of lime, with evolution of carbonic acid and hydrogen. The crude citrate of lime prepared in Sicily, and imported for the preparation of the acid, is found sometimes to undergo this change spontaneously, so that it has been

recommended to neutralise the hot lemon-juice with carbonate of magnesia (which is abundant in Italy), when the tribasic citrate of magnesia is precipitated in crystals. By dissolving this precipitate in a fresh quantity of hot lemon-juice, and evaporating, the bibasic citrate of magnesia is obtained in crystals, which is recommended as the best form in which to import the acid into this country.

429. *Malic acid* ($2HO . C_8H_4O_8$) is a crystalline acid found, as its name implies, in apples, and in many other fruits. It is present, together with oxalic acid, in rhubarb. Tobacco leaves also contain it in the form of bimalate of lime, $CaO . HO . C_8H_4O_8$.

In order to extract the malic acid from rhubarb stalks, it is converted into malate of lime, the solubility of which enables it to be separated from the insoluble citrate and tartrate of lime. The juice is squeezed out of the stalks by a press, nearly neutralised with slaked lime suspended in water, and chloride of calcium is added. The precipitate containing tartrate, citrate, phosphate, and oxalate of lime, is filtered off, and the liquid boiled down, when malate of lime ($2CaO . C_8H_4O_8$) is separated. This is washed and added to hot nitric acid, diluted with two measures of water, as long as it continues to be dissolved. On cooling, bimalate of lime ($CaO . HO . C_8H_4O_8$) is deposited, which is dissolved in water and decomposed by acetate of lead, when it gives a curious precipitate of malate of lead ($2PbO . C_8H_4O_8 . 6Aq.$), which becomes crystalline on standing, and fuses in the liquid below the temperature of boiling water. By suspending the malate of lead in water, and decomposing it with hydrosulphuric acid, the lead is separated as sulphide, and a solution of malic acid is obtained, which gives deliquescent prismatic crystals of the acid when evaporated to a syrup and set aside. Malic acid is decomposed by heat into two isomeric acids, the *malaic* and *fumaric* ($2HO . C_8H_2O_6$; the latter is found in the plant known as *fumitory* (*Fumaria officinalis*).

An excellent source of malic acid is the juice of the unripe berries of the mountain-ash, in which it is accompanied by a volatile oily acid of pungent aromatic odour; this has been called *parasorbic acid*, and has the formula $HO . C_{12}H_7O_3$. When fused with hydrate of potash, or boiled with a strong mineral acid, it suffers a remarkable conversion into a crystalline solid acid, having precisely the same composition, called *sorbic acid*.

Under the influence of yeast, in the presence of water, malate of lime is converted into succinate and acetate of lime—

$$\underset{\text{Malic acid.}}{3(2HO . C_8H_4O_8)} = \underset{\text{Succinic acid.}}{2(2HO . C_8H_4O_6)} + \underset{\text{Acetic acid.}}{HO . C_4H_3O_3} + 4CO_2 + 2HO.$$

The amide of malic acid, *malamide*, $C_8H_8N_2O_6$ (malate of ammonia, $2NH_4O . C_8H_4O_8$ *minus* 4HO), has attracted some attention, because it has the same composition as *asparagine*, a crystalline substance extracted from the juice of asparagus, marsh-mallow root, and some other plants; but it is not identical with it, though asparagine, when acted on by nitrous acid, yields malic acid—

$$\underset{\text{Asparagine.}}{C_8H_8N_2O_6} + 2NO_3 = \underset{\text{Malic acid.}}{2HO . C_8H_4O_8} + 2HO + N_4.$$

Asparagine is really the amide of another acid, the *aspartic*, into the ammonia-salt of which it becomes converted when heated for some time with water—

$$\underset{\text{Asparagine.}}{C_8H_8N_2O_6} + 2HO = \underset{\text{Aspartate of ammonia.}}{NH_4O . C_8H_3NO_7}.$$

430. *Tannic acid*, or *tannin* ($C_{54}H_{22}O_{34}$), the astringent principle of gall-nuts, from which it may be extracted by water, is characterised by

two very useful properties, viz., that of yielding a black precipitate with the salts of peroxide of iron, and of forming a tough insoluble compound with gelatine and gelatigenous membrane, the first being turned to account in the preparation of ink, and the second in that of leather.

For the preparation of ink, three quarters of a pound of bruised nut-galls are digested in a gallon of cold water, and six ounces of green vitriol (sulphate of iron) are added, together with six ounces of gum, and a few drops of kreasote. The mixture is set aside for two or three weeks, being occasionally agitated, and the ink afterwards poured off from the undissolved part of the nut-galls.

Pure sulphate of iron ($FeO . SO_3$) and tannic acid might be mixed without change; but when the mixture is exposed to the air, oxygen is absorbed, converting the protoxide of iron (FeO) into sesquioxide (Fe_2O_3), which combines with the tannic acid to form a black precipitate of tannate of sesquioxide of iron, the exact composition of which is not known. The gum is added to render the liquid viscous, so as to prevent the subsidence of the black precipitate, and the kreasote prevents the ink from becoming mouldy. The brown colour of the ink in old manuscripts is due to the tannic acid having been partly removed by oxidation, leaving the brown peroxide of iron; the stain of *iron-mould* left by ink on linen after washing is due to the entire removal of the tannic acid by the alkali in the soap.

Tanning.—When infusion of nut-galls is added to a solution of gelatine, the latter combines with the tannic acid, and a bulky precipitate is obtained. If a piece of skin, which has the same composition as gelatine, be placed in the infusion of nut-galls, it will absorb the whole of the tannic acid, and become converted into leather, which is much tougher than the raw skin, less permeable by water, and not liable to putrefaction.

The first operation in the conversion of hides into leather, after they have been cleansed, consists in soaking them for three or four weeks in pits containing lime and water, which saponifies the fat, and loosens the hair. The same object is sometimes attained by allowing the hides to enter into putrefaction, when the resulting ammonia has the same effect as the lime. The loosened hair having been scraped off, the hides are soaked for twelve hours in water containing $\frac{1}{100}$th of sulphuric acid, which removes adhering lime, and opens the pores of the skin, so as to fit it to receive the tanning liquid.

The tanning material generally employed for hides is the infusion of oak-bark, which contains *querci-tannic acid*, very similar in properties to tannic acid. The hides are soaked in an infusion of oak-bark for about six weeks, being passed in succession through several pits, in which the strength of the infusion is gradually increased. They are then packed in another pit with alternate layers of coarsely ground oak-bark; the pit is filled with water, and left at rest for three months, when the hides are transferred to another pit, and treated in the same way; but, of course, the position of the hides will be now reversed—that which was uppermost and in contact with the weakest part of the tanning liquor, will now be at the bottom. After the lapse of another three months the hides are generally found to be tanned throughout, a section appearing of a uniform brown colour. It has now increased in weight from 30 to 40 per cent. The chemical part of the process being now completed, the leather is subjected to certain mechanical operations to render it as desired. *Tanning the thinner kinds of leather, such*

sumach is used, which consists of the ground shoots of the *Rhus Co* and contains a large proportion of tannic acid.

Morocco leather is made from goat and sheep skins, which are de of hair by liming in the usual way, but the adhering lime is after removed by means of a bath of sour bran or flour. In order to t skin so prepared, it is sewn up in the form of a bag, which is fille infusion of sumach, and allowed to soak in a vat of the infusion fo hours. A repetition of the process, with a stronger infusion, is nec but the whole operation is completed in twenty-four hours. The are now washed and dyed, except in the case of red morocco, w dyed before tanning, by steeping it first in alum or chloride of t mordant, and afterwards in infusion of cochineal. Black morocco with acetate of iron, which acts upon the tannic acid. The anili are now much employed for dyeing morocco.

The *kid* of which gloves are made is not actually tanned, but ted to an elaborate operation called *tawing*, the chief chemical fe which are the removal of the excess of lime,* and opening the the skin by means of a sour mixture of bran and water, in whi acid is the agent; and the subsequent impregnation of the pe with chloride of aluminum, by steeping it in a hot bath contain and common salt. The skins are afterwards softened by knead mixture containing alum, flour, and the yolks of eggs. The put of the skin is as effectually prevented by the chloride of alumin tanning.

Wash leather and *buckskin* are not tanned, but *shamoyed*, w sists in sprinkling the prepared skins with oil, folding then *stocking* them under heavy wooden hammers for two or thr When the grease has been well forced in, they are exposed i atmosphere, to promote the drying of the oil by absorption (p. 581). These processes having been repeated the requisite n times, the excess of oil is removed by a weak alkaline bath, and are dried and rolled. The buff colour of wash-leather is impa weak infusion of sumach.

Parchment is made by stretching lamb or goat skin upon a moving the hair by lime and scraping, as usual, and afterward with pumice stone, until the proper thickness is acquired.

Tannic acid, like many other proximate constituents of (*see* p. 476), when boiled with diluted sulphuric acid, yields gr whilst a new acid may be obtained from the solution, which is gallic acid†—

$$\underset{\text{Tannic acid.}}{C_{54}H_{22}O_{34}} + 10HO = 3(\underset{\text{Gallic acid.}}{C_{14}H_6O_{10}}) + \underset{\text{Grape-sugar.}}{C_{12}H_{14}O_{14}}.$$

The addition of dilute sulphuric acid to the infusion of gall- duces a precipitate composed of tannic and sulphuric acids, dissolves when boiled with excess of sulphuric acid, suffering change.

431. *Gallic acid* ($3HO.C_{14}H_3O_7$) is also formed by the ox tannic acid when exposed to the air, particularly in the presen

* Polysulphides of sodium and calcium are sometimes employed for removin

† It will be perceived that tannic acid is analogous in constitution to the gl id mentioned at p. 578, which splits into grape-sugar and tartaric acid when luted sulphuric acid, exactly as tannic acid splits into grape-sugar and gallic

matters associated with it in the gall-nut, which seem to act like the ferment in the quick vinegar process (p. 492). The method generally practised for obtaining gallic acid consists in exposing powdered nut-galls in a moist state to the action of the air for some weeks, in a warm place, when oxygen is absorbed, and carbonic acid evolved, the powder becoming covered with crystals of gallic acid (tannic acid does not crystallise). By boiling the mass with water the gallic acid is extracted, and since, unlike tannic acid, it is very sparingly soluble in cold water, the greater portion crystallises out as the solution cools, in long silky needles, containing $C_{14}H_6O_{10} + 2Aq$.

In this process another acid is obtained in small quantity, which is insoluble in water, and has been called *ellagic acid* ($HO.C_{14}H_5O_8$); it possesses some interest, because it is found as a product of animal life in certain intestinal concretions or *bezoars*, occurring in the antelopes of Central Asia.

In most astringent substances a small quantity of gallic acid accompanies the tannic.

Gallic acid dissolves in oil of vitriol with a red colour, and when the solution is poured into water, a red-brown precipitate is obtained, called *rufigallic acid* ($C_{14}H_6O_6$), which is interesting from its property of dyeing calico red, if previously mordanted with alum.

When powdered nut-galls are heated in an iron pan surmounted with a cone of paper (*see* benzoic acid, p. 473) to about 420°, a quantity of crystals sublime into the cone, which are *pyrogallic acid* ($C_{12}H_6O_6$), or more properly, *pyrogalline*, for it is doubtful whether it is really an acid substance.

Its formation from the tannic acid of the galls is explained by the equation—

$$\underset{\text{Tannic acid.}}{C_{54}H_{22}O_{34}} + 2HO = 4\underset{\text{Pyrogallic acid.}}{(C_{12}H_6O_6)} + 6CO_2.$$

As its name implies, this acid may also be obtained by the action of heat upon gallic acid, which suffers a similar decomposition.*

This substance is extensively prepared for use in photography, in which art its great tendency to absorb oxygen is called into play, rendering it capable of decomposing the salts of silver with immediate separation of the metal.

The solution of pyrogallic acid soon becomes brown when exposed to the air, from absorption of oxygen, and if it be mixed with an alkali, it absorbs oxygen almost instantaneously, acquiring a very dark brown colour. This property renders pyrogallic acid very useful in the analysis of air and of other gases containing uncombined oxygen; a portion of air confined in a graduated tube over mercury (*see* fig. 73), is shaken with a strong solution of potash to absorb carbonic acid, and the diminution of volume having been noted, some solution of pyrogallic acid is introduced; on shaking for a few seconds, the oxygen is entirely absorbed, when the volume of the nitrogen may be observed.

The salts of tannic and gallic acids are not very known. The latter appears to be a tribasic acid, so that its formula would be $3HO.C_{14}H_3O_7$, the 3HO being replaceable by a

* By heating gallic acid under pressure with two or three times its weight of water to 410° F. for half-an-hour, and evaporating the solution, it is said that a large quantity of pyrogallic acid may be obtained.

The acid character of pyrogallic acid is very feeble.

The three acids are distinguished by their action upon the salts of iron. With pure protosulphate of iron ($FeO.SO_3$) neither tannic nor gallic acid gives any reaction, but pyrogallic acid gives a deep indigo blue solution, whilst with persulphate ($Fe_2O_3.3SO_3$) or perchloride (Fe_2Cl_3) of iron the two former give a bluish-black precipitate, and pyrogallic acid gives a bright red solution.

The presence of tannic acid in a vegetable infusion is easily recognised by the addition of perchloride of iron, but the hue which is produced is not the same in all astringent substances, because they contain different varieties of *tannin*.

All these varieties, however, differ from tannic acid properly so called, in not furnishing pyrogallic acid when heated.

The astringent principle of *catechu* and *kino*, which are used by tanners, is called *mimotannic acid*.

VEGETABLE ALKALOIDS.

432. In some plants the vegetable acids are combined with vegetable alkalies or alkaloids; thus, in opium, the morphine is combined with meconic acid; in cinchona bark, the quinine is combined with kinic acid. The methods adopted for the separation of these alkaloids from the acids and other substances associated with them are among the most important processes of practical chemistry.

Extraction of the alkaloids from opium.—Opium is the concrete milky juice which exudes on incising the unripe capsules of the *Papaver somniferum*, and is imported into this country from Persia, Turkey, Bengal, and Egypt, in the form of round masses or cakes enveloped in leaves; it has a dark colour, a soft waxy consistence, and a peculiar characteristic odour. Different samples vary much in composition, but the following result of an analysis of Smyrna opium will give an idea of the nature of this complex drug:—

100 *parts of Smyrna Opium contained—*

Gum,	26·2	Narcéine,	6·7
Caoutchouc,	6·0	Meconine,	0·8
Resin,	3·6	Codeine,	0·7
Oily matter,	2·2	Colouring and other organic matters,	19·1
Meconic acid,	5·0		
Morphine,	10·8	Water,	9·9
Narcotine,	6·8		

The medicinal value of opium appears to be due chiefly to the morphine ($C_{34}H_{19}NO_6$), which is present, for the most part, in the state of meconate of morphine; in order to obtain it in the separate state, the opium is cut into slices and digested with water at a moderate heat for two or three hours; the liquor is then strained and evaporated, a little chalk being added to neutralise the free acid. The concentrated solution, containing chiefly morphine and codeine, in combination with meconic and sulphuric acids, is mixed with solution of chloride of calcium, when the meconic acid is precipitated in combination with lime, carrying with it a great part of the colouring matter, and leaving in solution the hydrochlorates of morphine and codeine, which may be obtained in crystals by evaporation.

The hydrochlorates are decolorised with animal charcoal and recrystallised. On adding ammonia to the solution containing these salts, the morphine only is precipitated, and may be purified by crystallisation from alcohol, which deposits it in white rectangular prisms, having the formula $C_{34}H_{19}NO_6 + 2Aq$.

The solution from which the morphine has been precipitated still contains the hydrochlorate of codeine, and on decomposing it with potash, the codeine is precipitated in crystals, of the composition $C_{34}H_{21}NO_6 + 2Aq$.

The mother-liquor from the hydrochlorates of morphine and codeine contains narcotine, narcéine, meconine, thebaine, and paparverine, together with resin and colouring matter.*

The leading features of morphine are its sparing solubility in cold water, its bitter taste and alkaline reaction, and narcotic poisonous properties. It is generally identified by its giving an inky blue colour with perchloride of iron, and a golden yellow with nitric acid.

The *hydrochlorate of morphine* ($C_{34}H_{19}NO_6$. HCl), or *muriate of morphia*, is the chief form in which this alkaloid is used medicinally.

Narcotine ($C_{46}H_{25}NO_{14} + 2Aq$.) possesses some interest as having been the first base extracted from opium, whence it may be obtained by simply treating the drug with ether, in which the morphine is insoluble. The greater part of the narcotine is left in the residue after exhausting the opium with water, from which it is extracted by digestion with acetic acid; on neutralising the solution with ammonia, narcotine is precipitated. It is a weak base, and has no alkaline reaction.

The *meconic acid* which exists in opium is a tribasic acid, having the formula $3HO . C_{14}HO_{11}$; it is soluble in hot water, and crystallises on cooling in plates which contain six equivalents of water of crystallisation. It gives a blood-red colour with solution of perchloride of iron.

433. *Extraction of quinine.*—The *cinchona* or *Peruvian bark*, so highly prized for its medicinal qualities, is obtained chiefly from the districts around the Andes, and is imported in three varieties, of which the yellow cinchona is richest in quinine, the pale or grey bark in cinchonine, whilst the red bark contains both these bases in considerable quantity. The alkaloids are combined with *kinic acid*, and with a variety of tannin known as quinotannic acid.

In order to extract them, the bruised bark is boiled with diluted hydrochloric acid, and the filtered solution, containing the hydrochlorates of quinine and cinchonine, is mixed with enough lime diffused through water to render it alkaline. The quinine and cinchonine, which are very sparingly soluble in cold water (requiring about 400 times their weight to dissolve them), are precipitated together with some of the colouring matter of the bark.

The precipitate having been collected upon a linen strainer and strongly pressed, is treated with boiling alcohol, which dissolves both the alkaloids, leaving any excess of lime undissolved. A part of the alcohol is then recovered by distillation, and the solution containing the quinine and cinchonine is neutralised with sulphuric acid, so as to convert the alkaloids into sulphates, and is then decolorised with animal charcoal, and allowed to crystallise. Sulphate of quinine, being much less soluble in water than the sulphate of cinchonine, crystallises out first, leaving the latter in solution.

* *Κώδεια, a poppy head; νάρκη*, torpor; [illegible] πυ.

The sulphate of quinine is dissolved in water and decompo monia, when the quinine is separated as a white powder, whi dissolved in alcohol and crystallised.

The liquid from which the sulphate of quinine has been de tains, in addition to the sulphate of cinchonine, another base same composition as quinine, but distinguished from it by th tion of its sulphate to crystallise. This base is termed *quini* produced from quinine under the influence of an excess of aci most important constituent of the substance called *quinoidine* o *quinine*, which is prepared for sale from the mother-liquors of of quinine, and forms a cheap substitute for quinine in medici

Quinine crystallises in small prisms, which have the $C_{40}H_{24}N_2O_4 . 6Aq.$, and although sparingly soluble, even in b it has an extremely bitter taste, which is also possessed by its

Quinine is employed in medicine in the form of sulphate—

$$(C_{40}H_{24}N_2O_4 . HO . SO_3 + 7Aq.)$$

which requires as much as 700 parts of cold water to dissol readily dissolved in water acidulated with sulphuric acid, wh verted into the acid sulphate of quinine ($C_{40}H_{24}N_2O_4 . 2$ The solution is remarkable for its action upon light, for al perfectly colourless when held directly in front of the eye, if se it appears to have, especially at the edge, a beautiful pale This phenomenon, which is termed *fluorescence*, has been alre to in the case of other substances (p. 478).

Quinic or *kinic acid.*—By evaporating the infusion of ci from which the quinine and cinchonine have been separat crystals of kinate of lime are obtained, and by decomposing sulphuric acid, the *kinic acid* ($2HO . C_{28}H_{20}O_{20}$) passes into solu it may be obtained in prismatic crystals.

This acid is chiefly interesting on account of the peculiar some of its derivatives. When distilled with sulphuric acid a of manganese, the oxygen evolved from the mixture conve acid into a new substance, which condenses in beautiful yel called kinone—

$$\underset{\text{Kinic acid.}}{2HO . C_{28}H_{20}O_{20}} + O_8 = \underset{\text{Kinone.}}{2(C_{12}H_4O_4)} + 4CO_2 +$$

The same substance is obtained in a similar manner fron constituents of the coffee-berry (caffeic or caffeotannic acid). ing kinone in water containing sulphurous acid gas, and eva solution, colourless crystals of *hydrokinone* are obtained—

$$\underset{\text{Kinone.}}{C_{12}H_4O_4} + 4HO + 2SO_2 = \underset{\text{Hydrokinone.}}{C_{12}H_6O_4} + 2(H$$

When a solution of kinone is mixed with one of hydroki ful green crystals are deposited, which are known as *green* ($C_{12}H_4O_4 . C_{12}H_6O_4$), and may also be obtained by the action agents, such as ferric chloride, upon hydrokinone. When ki on with hydrochloric acid and chlorate of potash, it is con yellow crystalline body, known as *perchlorokinole* or *chlorani* which is also obtained in a similar way from aniline, salic tine. Potash dissolves it when heated, giving a purple solut

Theine or *caffeine—Tea—Coffee.*—A very remarkable instance of lication of chemistry to explain the use of widely different articles by different nations, with a view to the production of certain is effects upon the system, is seen in the case of coffee, tea, Para-, and the *kola-nut* (of Central Africa), which are very dissimilar sensible properties, and afford little or no gratification to the owing what attractions they possess chiefly to the presence, in one and the same active principle or alkaloid, which has a effect upon the animal economy. This alkaloid is known as or theine, and is associated in the three articles of diet men-bove, with various substances, which give rise to their diversity ir.

raw coffee-berry presents, on the average, the following composi-

100 *parts of Raw Coffee contain—*

Woody fibre,	34·0
Water,	12·0
Fat,	12·0
Cane sugar and gum,	15·5
Legumine, or some allied substance,	13·0
Caffeine,	1·5
Caffeic acid,	4·0
Mineral substances,	7·0

the raw berry is treated with hot water, the infusion, which con-e sugar and gum, the legumine, caffeine, and *caffeic acid* ($C_{14}H_8O_7$), e of the peculiar fragrance which distinguishes the ordinary be-nd is due to an aromatic volatile oily substance termed *caffeone*, luring the roasting to which the berry is subjected before use. latile oil, which is present in very minute quantity, is produced e of the soluble constituents of the berry (probably from the id), for if the infusion of raw coffee be evaporated to dryness, lue, when heated, acquires the characteristic odour of roasted

oasting is effected in ovens at a temperature rather below 400° F., e berry swells greatly, and loses about $\frac{1}{5}$th of its weight, becoming nd easily ground to powder. It also becomes very much darker r, from the conversion of the greater part of its sugar into caramel , which imparts the dark-brown colour to the infusion of coffee. asting be carried too far, a very disagreeable flavour is imparted to e by the action of heat upon the legumine and other nitrogenised es contained in the berry.

100 parts of the roasted coffee, boiling water extracts about 20 nsisting of caffeine, caffeic acid, caramel, legumine, a little sus-fatty matter, fragrant volatile oil (caffeone), and salts of potash ly the phosphate). The undissolved portion of the coffee contains, ne woody fibre, a considerable quantity of nitrogenised (and nutri-atter, and hence the custom, in some countries, of taking this together with the infusion.

ler to extract the caffeine from the infusion of coffee, it is mixed ution of tribasic acetate of lead, to precipitate the caffeic acid and the colouring matter. Through the filtered solution, sulphuretted n is passed to remove the lead as sulphide, and the liquid filtered

from this is evaporated to a small bulk, when the caffeine crystalli in white silky needles, which have a bitter taste, and the com $C_{16}H_{10}N_4O_4 . 2HO$. Its basic properties are very feeble.

The constituents of the leaves of the tea-plant (*Thea Sinensis*) a general similarity to those of the coffee-berry. In the fresh leaf, in addition to the woody fibre, a large quantity of a substance co nitrogen, an astringent acid similar to tanni small quantity of caffeine, and some mineral constituents.

The aroma of tea does not belong to the fresh leaf, but is produ that of coffee, during the process of drying by heat, which de small quantity of a peculiar volatile oil, having powerful stimula perties. The freshly-dried leaf is comparatively so rich in that it is not deemed advisable to use it until it has been kept time.

Green and black tea are the produce of the same plant, the being caused by the mode of preparation. For green tea the dried over a fire as soon as they are gathered, whilst those in black tea are allowed to remain exposed to the air in heaps hours, and are then rolled with the hands and partially dried these processes being repeated three or four times to develope flavour. The black colour appears to be due to the action of t the tannin present in the leaf.

Boiling water extracts about 30 parts of soluble matter f black tea, and 36 from 100 of green tea. The principal con the infusion of tea are tannin, aromatic oil, of which green t about 0·8 and black tea 0·6 per cent., and caffeine, the p which, in the dried leaf, varies from 2·2 to 4·1 per cent., bein larger quantity in green tea.

The spent leaves contain the greater part of the legumine, siderable quantity of caffeine, which may be extracted by b with water, and treating the decoction as above recommended of coffee.

If tea be boiled with water, the solution precipitated w acetate of lead, the filtered liquid evaporated to dryness, and cautiously heated, the caffeine sublimes in beautiful crystals.

Cocoa and *chocolate* are prepared from the cacao-nut, w seed of *Theobroma Cacao*, and is characterised by the prese than half of its weight (*minus* the husk) of a fatty substanc *cacao-butter*, and consisting of oleine and stearine, which does rancid like the natural fats generally. The cacao-nut also large quantity of starch, a nitrogenised substance resembling gether with gum, sugar, and *theobromine*, a feeble base ver caffeine, but having the composition $C_{14}H_8N_4O_4$.

The seeds are allowed to ferment in heaps for a short time proves their flavour, dried in the sun and roasted like coffe velopes the peculiar aroma of cocoa. The roasted beans h crushed and winnowed to separate the husks, are ground in in which the fatty matter melts and unites with the ground paste, which is mixed with sugar and pressed into moulds. paration of chocolate, vanilla and spices are also added.

From the composition of cocoa and chocolate it is seen tha med, as is usual, in the form of a paste, they would pro tritious than mere infusions of tea and coffee.

e appears to be a methylated derivative from theobromine, for when it is h potash, methylamine is evolved, and by acting with iodide of methyle pon a silver-compound obtained from theobromine, $C_7(H_3Ag)N_4O_2$, the d methyle change places, yielding AgI and caffeine, $C_8H_3(CH_3)N_4O_2$, or theobromine.

The vegetable alkali *strychnine* ($C_{42}H_{44}N_2O_4$), only too well known activity as a poison, is contained in *crow-fig* or *Nux-vomica*, the the poison-nut tree of the East Indies, and in several other plants same family. The strychnine appears to be combined, in the nux-a, with lactic acid, and is accompanied by a second alkaloid, *brucine* ($C_{46}N_2O_4$). In order to extract it, the bruised seeds are boiled with acidulated with hydrochloric acid, the solution is strained, and ren-l alkaline by adding hydrate of lime, which displaces the strychnine brucine from their combination with the acid, and separates them in form of a precipitate. When this is boiled with alcohol, the excess of e remains undissolved, whilst the strychnine and brucine are carried o solution; and since the former is less soluble in alcohol than the ter, it is deposited, before the brucine, on evaporating the liquid, in the m either of octahedral or prismatic crystals, which have an intensely ter taste. This remarkable bitterness is one of the most prominent aracters of strychnine; for although 7000 parts of water are required to solve one part of this alkaloid, the solution possesses an intolerably tter flavour, even when further diluted with 100 times its weight of ater. Chloroform and benzole both dissolve strychnine with great ease; d since these liquids refuse to mix with water, they are often employed extract the poison from a large bulk of aqueous liquid by agitating it th a small quantity of one of them, which is then separated from the ater and evaporated, in order to obtain the strychnine in the solid form. ery minute quantities may then be identified by moistening with strong lphuric acid, and adding a minute quantity of chromate of potash, when e chromic acid acts upon the strychnine, giving rise to products of oxida-on, which pervade the liquid in the form of beautiful purple streaks.

Curarine, $C_{20}H_{15}N$, is a crystalline alkaloid which has been extracted om the woorari or curara poison employed by the American Indians for oisoning arrows. It dissolves easily in water and alcohol, but not in her. Strong sulphuric acid gives it a fine blue colour.

436. Tobacco owes its active character chiefly to the presence of a vege-ble alkali which is not found in any other plant than the *Nicotiana bacum*, from the leaf of which the various forms of tobacco are manu-ctured. This alkali, *nicotine* ($C_{10}H_7N$), is distinguished from most thers by the absence of oxygen, and by its liquid condition at the ordi-ary temperature.

In order to extract the nicotine from tobacco, the leaves are boiled with ater, which dissolves the alkaloid, in combination with malic and citric cids. The liquid, having been strained, is evaporated to a syrup and ixed with alcohol, when it separates into two layers, of which the pper contains the salts of nicotine dissolved in alcohol, the lower aqueous yer retaining the greater part of the extraneous vegetable matters. The lcoholic layer having been drawn off, is next shaken with potash, to ombine with the acids, and with ether to dissolve the nicotine then se ee. On decanting the ethereal solution of nicotine which rises to th rface, and evaporating the ether, the nicotine is left in the form of n ily liquid, which is colourless when perfectly pure, but soon acquires

dark brown colour when exposed to the air. It is very readily distinguished by its very pungent, irritating odour, recalling that of tobacco, and which is very perceptible at the common temperature, although the boiling point of nicotine is so high as 480° F. Water, alcohol, and ether dissolve nicotine with facility. The poisonous action of this alkaloid upon animals is very powerful, death almost immediately following its administration. The Virginia tobacco contains more nicotine than other varieties, the alkaloid amounting to nearly 7 per cent. of the weight of the leaf dried at 212° F., whilst the Maryland and Havannah varieties contain only 2 or 3 per cent. of nicotine. Tobacco is remarkable for the very large amount of ash which it leaves when burnt, amounting to about one-fifth of the weight of the dried leaf, and containing about one-third of carbonate of potash, resulting from the decomposition of the malate, citrate, and nitrate of potash during the combustion. The presence of this latter salt in large quantity (3 or 4 parts in 100 of the dried leaf) distinguishes tobacco from most other plants, and accounts for the peculiar smouldering combustion of the dried leaves.

Cigars are made directly from the tobacco leaves, which are only moistened with a weak solution of salt in order to impart the requisite suppleness; but *snuff*, after being thus moistened, is subjected, in large heaps, to a fermentation extending over eighteen or twenty months, which results in its becoming alkaline from the development of carbonate of ammonia (by the putrefaction of the vegetable albumen in the leaf) and of a minute quantity of free nicotine, which imparts the peculiar pungency to this form of tobacco. The aroma of the snuff appears to be due to the production of a peculiar volatile oil during the fermentation. The proportion of nicotine in snuff is only about two per cent., being one-third of that found in the unfermented tobacco; and a great part of this exists in the snuff in combination with acetic acid, which is also a result of the fermentation. It is also not improbable that a little acetic ether is produced, and perhaps some other acids and ethers of the acetic series (*e.g.*, butyric and valerianic), of which extremely minute quantities would give rise to great differences in the aroma of the snuff.

VEGETABLE COLOURING MATTERS.

437. Notwithstanding the great variety and beauty of the tints exhibited by plants, comparatively few yield colouring matters which are sufficiently permanent to be employed in the arts, the greater number of them fading rapidly as soon as the plant dies, since they are unable to resist the decomposing action of light, oxygen, and moisture, unless supported by the vital influence in the plant, some of them even fading during the life of the plant, as may be seen in some varieties of the rose, which are only fully coloured in those parts which have been partly obscured.

The green colouring matter of plants has been termed *chlorophyll*,* and is a resinous substance containing carbon, hydrogen, nitrogen, and oxygen, which has never yet been obtained in so pure a condition that its composition could be accurately determined, since it cannot be crystallised or distilled, and is therefore not amenable to the usual methods by which organic substances are obtained in a pure state.

When green leaves are boiled with alcohol, the latter acquires a fine green colour, and, when evaporated, deposits the chlorophyll. When the

* Χλωρός, green; φύλλον, a leaf.

coholic solution of chlorophyll is boiled with alcoholic solution of otash, and hydrochloric acid afterwards added, a yellow precipitate (*phyl-xanthine*) is obtained, and a fine blue colouring matter (*phyllocyanine*) mains in solution. The blue matter contains nitrogen, and both are soluble in water. The autumnal colour of leaves may possibly be due o the disappearance of the phyllocyanine. On immersing green leaves in hlorine they assume an autumnal tint.

The blue colouring matter contained in many flowers, such as the violet, as been named *cyanine*. Acids change its blue colour to red, and hence he blue colour is exhibited only by flowers the juice of which is neutral, whilst red flowers yield an acid juice. The colouring matter of grapes nd of red wine appears to be identical with cyanine.

Two yellow colouring matters have been extracted from flowers, and ave been named *xanthine* and *xanthéine*, the latter being soluble in vater.

Saffron is a yellow colouring matter obtained from the flowers of the *Crocus sativus*, which are themselves of a blue colour, but have yellow nthers. When these are dried and pressed into cakes, they form the affron of commerce, which is characterised by its very remarkable and omewhat agreeable odour. The yellow colouring matter is readily dis-olved by water and alcohol, but its chemical composition has not been letermined.

Safflower consists of the petals of the *Carthamus tinctorius*, a plant ultivated in Egypt. It furnishes a red colouring matter called *cartha-nine* ($C_{28}H_{16}O_{14}$), which is used in dyeing, although it fades easily when xposed to light. It exhibits the characters of an acid, being dissolved y alkalies and reprecipitated by acids, a circumstance which is taken dvantage of in extracting it from the safflower.

The orange-yellow colouring matter known as *annatto* is extracted from he seeds of the *Bixa Orellana*, a native of the West Indies. The colouring rinciple has been called *bixine*, and is dissolved by alkalies, but precipi-ated again by acids. Annatto is used for colouring butter and cheese.

A valuable yellow colour is obtained from the *weld*, or *Reseda luteola*, by oiling the dried leaves with water. This colouring matter is termed *uteoline* ($C_{30}H_{14}O_{6}$), and may be sublimed in yellow needles.

The woods of various trees, when boiled with water, furnish colouring natters of considerable importance; thus, the wood of *Morus tinctoria*, or *ustic*, a West Indian tree, yields a crystalline yellow colour called *mori-annic acid* ($C_{26}H_{15}O_{20}$),

Logwood is the wood of the *Hæmatoxylon Campechianum*, which grows t Campeachy, in the Bay of Honduras. Its most important constituent s a yellow colouring matter called *hæmatoxyline*, which may be obtained n needle-like crystals having the composition ($C_{32}H_{14}O_{18}$, 2Aq.) It be-omes intensely red in contact with alkalies and oxygen, from the formation f hæmatein ($C_{32}H_{12}O_{12}$). Chromate of potash gives an intense black olour with infusion of logwood, which has been used as an ink, but is not ermanent.

Brazil wood, which is employed in the preparation of red ink, contains colouring matter somewhat resembling that of logwood.

The well-known Turkey red colour is obtained from *madder*, the root f the *Rubia tinctorum*, imported from the south of France and the evant. This root does not contain any red colouring matter during the *ife of the plant, but a yellow substance (rubian,* $C_{56}H_{34}O_{30}$), from the dece

position of which the madder red is obtained. There are several m in use for obtaining the red colour from madder. If the root be s in water for some time, so that some of the nitrogenised constituents to undergo decomposition, a peculiar fermentation is excited in the resulting in its decomposition into several new bodies, the chief of are a red crystalline colouring matter, *alizarine* ($C_{14}H_8O_4 . 3Aq$), uncrystallisable sugar. The alizarine may be dissolved out either or alcohol, and may be obtained in beautiful plates having a golde

If the madder root be boiled with water, the rubian is dissol when this solution is boiled with dilute sulphuric acid, the rubia goes a decomposition similar to that mentioned above, and the being insoluble in the dilute acid, is precipitated.

Madder, which has been treated with hot sulphuric acid, so as t pose the rubian, is used in print-works under the name of *garan* yields a red solution containing alizarine when boiled with wate

Turmeric is the root of an East Indian plant, the *Curcuma l* colouring matter, called *curcumine*, is nearly insoluble in wate solves in alcohol. Its yellow colour is changed to brown b which leads to its use in the laboratory as a test of alkalinity.

438. *Litmus*, *archil*, and *cudbear* are brilliant, though not manent purple and violet colours, prepared from various liche *Roccella tinctoria* (litmus), and *Lecanora tartarea* (cudbear*).

Archil and cudbear owe their colour chiefly to the presence ($C_{14}H_7NO_6$), which does not exist ready formed in any of the l is developed during the preparation which they undergo.

If either of the above lichens be digested for some hours wit water, and the filtered solution be neutralised with hydrochl white gelatinous precipitate is obtained, which dissolves in b and is deposited in crystals on cooling. This substance m according to the particular lichen employed, of one or more acid of which have been named *erythric* ($C_{22}H_{16}O_{16}$), *evernic* (HO . and *lecanoric* ($C_{28}H_{14}O_{14}$) acids. These acids are remarkable for with which they furnish compound ethers when boiled with al

When either of these acids is boiled with an excess of lime o is decomposed, and if the excess of base be removed by carbon filtered liquid evaporated to a syrup, and extracted with boili the latter deposits prismatic crystals of *orcine* ($C_{14}H_8O_4 . 2$ formation of this body will be understood from the following e

$$\underset{\text{Erythric acid.}}{C_{32}H_{16}O_{16}} + 4CaO = 4(CaO . CO_2) + 2(\underset{\text{Orcin}}{C_{14}H_{}}$$

$$\underset{\text{Evernic acid.}}{C_{34}H_{16}O_{14}} + 2(CaO . HO) = 2(CaO . CO_2) + \underset{\text{Evernesic acid.}}{C_{18}H_{10}O_8} +$$

Pure orcine is a colourless substance, but when exposed to the j of ammonia and air, it is converted into a beautiful red colouri *orcéine*—

$$\underset{\text{Orcine.}}{C_{14}H_8O_4} + NH_3 + O_6 = \underset{\text{Orcéine.}}{C_{14}H_7NO_6} + 4H$$

Orcéine does not crystallise, and dissolves to a slight extent onl

* Said to have been named after Cuthbert, a manufacturer of the d

readily in alcohol and in alkaline liquids, yielding, in the latter case, eautiful purple solution, which becomes red when mixed with acids, and osits red flakes of orcéine.

The chemistry of the processes by which archil and cudbear are pre- ed will now be easily understood. The powdered lichen is mixed with ne (to furnish ammonia) and lime, and exposed to the air for some eks, when the lime decomposes the erythric and other acids, with forma- n of orcine, which then passes into orcéine under the influence of the mmonia and atmospheric oxygen.

The preparation of litmus from the *Roccella tinctoria* is similar to that st described, but a mixture of carbonate of ammonia and carbonate of otash is employed instead of the urine and lime. The chemical change hich takes place, although similar in principle, is not precisely identical ith the foregoing, for the principal colouring matter developed appears o be a red substance called *azolitmine* ($C_{18}H_{16}NO_{10}$), which differs from rcéine by its insolubility in alcohol. It dissolves in alkaline solutions with a beautiful blue colour, which is immediately reddened by acids, a roperty frequently turned to account by the chemist for detecting the cid reaction. Litmus occurs in commerce in small cakes, which are made p with chalk.

Erythrite ($C_8H_{10}O_8$) is a crystalline substance extracted from various lichens and fungi, which forms combinations with the fatty acids similar to those formed by glycerine. It is sometimes represented as a tetratomic alcohol (p. 562), $(C_8H_6)''''H_4 . O_8$.

439. *Indigo blue* ($C_{16}H_5NO_2$) is prepared from various species of *Indigofera*, grown in China, India, and America. The plants are covered with cold water and allowed to ferment; as soon as a blue scum appears upon the surface, a little lime is added and the mixture stirred briskly for some time, when the indigo is deposited in a pulverulent form; it is collected on calico strainers, pressed, and cut up into cakes.

The theory of the process is not yet clearly explained; it is certain that the indigo blue does not pre-exist in the plant, but is a product of the fermentation. Recent observations have shown that the indigo plants probably contain a substance called *indican* ($C_{52}H_{33}NO_{36}$), which stands in a similar relation to indigo blue to that in which rubian stands to alizarine (in the case of madder); it is soluble in water, and when heated with an acid, splits up into indigo blue, *indigo red*, and a peculiar uncrystallisable sugar. The indigo red may be extracted from commercial indigo by boiling with alcohol, in which the indigo blue is insoluble. Since indigo blue is insoluble in all ordinary solvents, it is necessary, in order to use it for dyeing, to reduce it to the condition of *white indigo*, which is soluble in alkalies.

If 2 parts of protosulphate of iron (copperas) be dissolved in 200 parts of water, and well shaken in a stoppered bottle with 1 part of powdered indigo and 3 of slaked lime, the indigo will disappear, and on allowing the precipitate to subside, a yellow fluid will be obtained, which becomes blue at the surface as soon as it is exposed to air. If this solution be mixed with hydrochloric acid, out of contact with air, a flocculent precipitate of *white indigo* is obtained. The composition of this substance $C_{16}H_6NO_2$, and it is formed from blue indigo ($C_{16}H_5NO_2$) by the addit an atom of hydrogen derived from water, the oxygen of which b bined with the protoxide of iron; one portion of the lime combi

the sulphuric acid of the sulphate of iron, whilst another serves to dissolve the white indigo, which is soluble in alkaline liquids—

$$FeO.SO_3 + CaO.HO = FeO.HO + CaO.SO_3,$$

$$2(FeO.HO) + HO + \underset{\text{Blue indigo.}}{C_{16}H_5NO_2} = Fe_2O_3.2HO + \underset{\text{White indigo.}}{C_{16}H_7NO_2}.$$

The solution of white indigo prepared by this process is employed for dyeing linen and cotton, which are immersed in the vat, and then exposed to the air, the oxygen of which removes an atom of hydrogen from the white indigo, and the blue indigo thus formed is precipitated upon the fibre.

Other reducing agents are sometimes substituted for the protosulphate of iron. Even decaying vegetable matter effects the conversion of blue into white indigo in an alkaline liquid. Thus, for some purposes, the vat is prepared by fermenting a mixture of indigo, madder, carbonate of potash, and lime, when the hydrogen extricated in the fermentation of the vegetable matter converts the blue into white indigo, which is then dissolved by the potash liberated from the carbonate by the lime.

When cloth is dyed with indigo (Saxony blue) the colour is dissolved by means of sulphuric acid. Fuming sulphuric acid dissolves indigo blue very readily, but oil of vitriol does not act quite so well. The solution thus obtained is commonly called *sulphindigotic acid*, but it really contains two acids, the *sulphindylic* ($HO.C_{16}H_4NO.2SO_3$) and *hyposulphindigotic*.

On heating indigo, it evolves purple vapours, which condense in prismatic crystals of a coppery lustre, consisting of pure *indigotine* or indigo blue ($C_{16}H_5NO_2$), which may be obtained in larger quantity by digesting indigo with grape-sugar, caustic soda, and weak alcohol, when a solution of white indigo is obtained which deposits the crystallised indigotine on exposure to air.

440. *Animal colouring matters.*—From the animal kingdom only two colouring matters of any great importance are derived, viz., cochineal and lac, both which are obtained from insects of the *coccus* tribe. The colouring matter of cochineal is known as *carmine*, and may be extracted from the insects by water or alcohol. It has acid properties, and has been named *carminic acid* ($C_{28}H_{14}O_{16}$). *Carmine-lake* is a combination of this acid with alumina, precipitated when a solution of alum and an alkaline carbonate are added to one of cochineal.

Dyeing and Calico-Printing.

441. The object of the dyer being to fix certain colouring matters permanently in the fabric, his processes would be expected to vary with the nature of the latter and of the colour to be applied to it. In order that uniformity of colour and its perfect penetration into the fibre may be attained, it is evident that the colouring matter must always be employed in a state of solution; and it must be rendered *fast*, or not removable by washing, by assuming an insoluble condition in the fibre. The simplest form of dyeing is that in which the fibre itself forms an insoluble compound with the colouring matter. Thus, if a skein of silk be immersed in a solution of indigo in sulphuric acid, it removes the whole of the colouring matter from the liquid, and may then be washed with water without losing colour; but if the same experiment be tried with cotton, he indigo will not be withdrawn from the solution, and when the cotton

s been well squeezed and rinsed with water, it will become white again. may be stated generally, that the animal fabrics (silk and wool) will sorb and retain colouring matters with much greater facility than getable fabrics (cotton and linen). In the absence of so powerful an traction between the fibre and the colouring matter, it is usual to impreg- te the fabric with a *mordant* or substance having an attraction for the lour, and capable of forming an insoluble combination with it, so as to tain it permanently attached to the fabric. Thus, if a piece of cotton boiled in a solution of acetate of alumina, the alumina will be precipi- ted in the fibre; and if the cotton be then soaked in solution of chineal or of logwood, the red colouring matter will form an insoluble mpound (or *lake*) with the alumina, and the cotton will be dyed of a st red colour.

Another method of fixing the colour in the fabric consists in impregnat- ng the latter with two or more liquids in succession, by the admixture of which the colour may be produced in an insoluble state. If a piece of any stuff be soaked in solution of perchloride of iron, and afterwards in ferrocyanide of potassium, the Prussian blue which is precipitated in the fibre will impart a fast blue tint.

An indispensable preliminary step to the dyeing of any fabric is the removal of all natural grease or colouring matter, which is effected by processes varying with the nature of the fibre, and is preceded, in the cases of cotton and woollen materials which are to receive a pattern, by certain operations of shaving and singeing for removing the short hairs from the surface.

From linen and cotton, the extraneous matters (such as grease and resin) are generally removed by weak solutions of carbonate of potash or of soda, and the fabrics are afterwards bleached by treatment with chloride of lime (p. 145). But since the fibres of silk and wool are much more easily injured by alkalies and by chlorine, greater care is requisite in cleansing them. Silk is boiled with a solution of white soap to remove the *gum*, as it is technically termed; but the natural grease is extracted from wool by soaking at a moderate temperature in a weak bath either of soap or of ammoniacal (putrefied) urine. Both silk and wool are bleached by sulphurous acid (p. 197).

Among the red dyes the most important are madder, Brazil wood, cochineal, lac, and the colours derived from aniline.

In dyeing red with madder or Brazil wood, the linen, cotton, or wool is first mordanted by boiling in a solution containing alum and bitartrate of potash, when it combines with a part of the alumina, and on plunging the stuff into a hot infusion of madder, the colouring matter forms an insoluble combination with that earth.

To dye Turkey-red, the stuff is also mordanted with alum, but has previously to undergo several processes of treatment with oil and with galls, the necessity of which is satisfactorily established in practice, though it is not easy to explain their action. The colour is finally brightened by boiling the stuff with chloride of tin.

Woollen cloth is dyed scarlet with lac or cochineal, having been mordanted by boiling in a mixture of bichloride of tin and bita potash.

The aniline colours (*see* p. 456) are d for dyeing silk either without any mordant or with t lbumen.

Blues are generally dyed with indig with Prus

the latter case the stuff is steeped successively in solutions of a salt of peroxide of iron and of ferrocyanide of potassium. Aniline blue is also much employed for silk and woollen fabrics.

The principal yellow dyes are weld, quercitron, fustic, annatto, chrysaniline, and chromate of lead. For the four first colouring matters aluminous mordants are generally applied. Chromate of lead is produced in the fibre of the stuff, which is soaked for that purpose, first in a solution of acetate or nitrate of lead, and then in chromate of potash.

Carbazotic acid (p. 461) is also sometimes employed as a yellow dye.

In dyeing blacks and browns, the stuffs are steeped first in a bath containing some form of tannin (p. 590), such as infusion of galls, sumach or catechu, and afterwards in a solution of a salt of iron, different shades being produced by the addition of indigo, of sulphate of copper, &c.

442. The art of calico-printing differs from that of dyeing, in that the colour is required to be applied only to certain parts of the fabric, so as to produce a pattern or design either of one or of several colours.

A common method of printing a coloured pattern upon a white ground consists in impressing the pattern by passing the stuff under a roller, to which an appropriate mordant thickened with British gum (p. 486) is applied. The stuff is then *dunged*, *i.e.*, drawn through a mixture of cow-dung and water, which appears to act by removing the excess of the mordant, and afterwards immersed in the hot dye-bath, when the colour becomes permanently fixed to the mordanted device, but may be removed from the rest of the stuff by washing.

If the pattern be printed with a solution of acetate of iron, and the stuff immersed in a madder-bath, a lilac or black pattern will be obtained according to the strength of the mordant employed. By using acetate of alumina as a mordant, the madder-bath would give a red pattern.

A process which is the reverse of this is sometimes employed, the pattern being impressed with a *resist*, that is, a substance which will prevent the stuff from taking the colour in those parts which have been impregnated with it. For example, if a pattern be printed with thickened tartaric or citric acid, and the stuff be then passed through an aluminous mordant, the pattern will refuse to take up the alumina, and subsequently, the colour from the dye-bath. Or a pattern may be printed with nitrate of copper, and the stuff passed through a bath of reduced indigo (p. 603), when the nitrate of copper will oxidise the indigo, and by converting it into the blue insoluble form, will prevent it from sinking into the fibre on those parts to which the nitrate has been applied, whilst elsewhere, the fibre, having become impregnated with the white indigo, acquires a fast blue tint when exposed to the air.

Sometimes the stuff is uniformly dyed, and the colour discharged in order to form the pattern. A white pattern is produced upon a red (madder) or blue (indigo) ground by printing with a thickened acid discharge, and passing the stuff through a weak bath of chloride of lime, which removes the colour from those parts only which were impregnated with the acid (p. 145). By adding nitrate of lead to the acid discharge, and finally passing the stuff through solution of chromate of potash, a yellow pattern (chromate of lead) may be obtained upon the madder red ground.

By applying nitric acid as a discharge, a yellow pattern may be obtained on an indigo ground (p. 125).

brilliant designs are produced by mordanting the stuff in a solu- stannate of potash or soda (p. 388), and immersing it in dilute sul- acid, which precipitates the stannic acid in the fibre. When the ed colouring matters are printed on in patterns, and exposed to the of steam, an insoluble compound is formed between the colour and nic acid, which usually exhibits a very fine and permanent colour. evident that by combining the principles of which an outline has n given, the most varied parti-coloured patterns may be printed.

ANIMAL CHEMISTRY.

Our acquaintance with the chemistry of the substances composing ies of animals is still very limited, although the attention of many lished investigators has been directed to this branch of the science. sons for this are to be found, firstly, in the susceptibility to change ed by animal substances when removed from the influence of life; ondly, in the absence, in such substances, of certain physical pro- by which we might be enabled to separate them from other bodies hich they are associated, and to verify their purity when obtained arate state. Two of the most important of these properties are ty and the tendency to crystallise. When a substance can suffer ion without change, it will be remembered that its boiling point a criterion of its purity; or if it be capable of crystallising, this taken advantage of in separating it from other substances which ise more or less easily than itself, and its purity may be ascertained e absence of crystals of any other form than that belonging to the ce. But the greater number of the components of animal frames can be crystallised nor distilled, so that many of the analyses which een made of such substances differ widely from each other, because lyst could never be sure of the perfect purity of his material; and hen concordant results have been obtained as to the percentage ition of the substance, the atomic formula deduced from it has been ngular and exceptional a character as to cast very strong suspicion he purity of the substance.

rdingly, the chemical formulæ of a great many animal substances fectly unintelligible, conveying not the least information as to the n in which the compound stands with respect to other substances, changes which it might undergo under given circumstances.

as been shown in the previous chapters of this work that we are ly learning to class all compound bodies under a few typical forms, the chemical properties of any substance may in many cases be ed from its composition as indicating the type to which it belongs. or example, the class of alcohols ($C_{2n}H_{2n+2}O_2$), or of volatile acids O_4), or of ammonias (XY_3), and it will be seen that even those e which are apparently the most complex, are perfectly intelligible eferred to their proper type (p. 542). But the extraordinary for- for example, deduced from the ultimate analysis of

Albumen,	$C_{216}H_{169}N_{27}O_{68}S_2$ and
Caseine,	$C_{185}H_{223}N_{36}O_{90}S_2$

be referred to any known type, and refuse to other ces, even if a type were invented expressly

Animal chemistry is for the above reasons in a very backward as compared with vegetable and mineral chemistry, though an ob of the progress of research affords us the consolation, that a steady is being made towards a generalisation of the facts which have b covered, especially by analogical reasoning from those two other ments of the science.

MILK.—The chemistry of milk is well adapted to introduce th of animal chemistry, because that liquid contains representatives of substances which make up the animal frame; and it is on this that it occupies so high a position among articles of food.

Although, to the unaided eye, milk appears to be a perfectly geneous fluid, the microscope reveals the presence of innumerable floating in a transparent liquid, which is thus rendered opaque. be very violently agitated for several hours, masses of an oily fat p. 582) are separated from it, and leave the liquid transparent. was originally distributed throughout the milk in minute globules in very thin membranes, which were torn by the violent agitat the fatty globules then cohered into larger masses.

For the preparation of butter, it is usual to allow the milk to some hours, when a layer of *cream* collects upon the surface, the p of which is very variable, but is generally about $\frac{1}{15}$th of the volu milk. This cream contains about 5 per cent. (by weight) of cent. of caseine, and water. When the cream is *churned*, the membranes of the fat globules are broken, and the fat unites in solid mass of butter, from which the butter-milk containing th may be separated. If this be not done effectually, the casein left in the butter, being a nitrogenised substance, will soon begin pose, and will induce a decomposition in the butter (p. 582), r the elimination of certain volatile acids, which impart to it a offensive taste and odour. To prevent this, salt is generally butter which has been less carefully prepared, in order to p caseine from decomposition.

Pure butter is essentially a mixture of margarine and oleine w quantities of other fats, such as butyrine, caprine, and caproi

Fresh milk is slightly alkaline to test-papers, but after a sl acquires an acid reaction; and if it be then heated, it coagulat separation of the caseine. This spontaneous acidification of mi by the fermentation of the *sugar of milk*, under the influence of which results in the production of *lactic acid*, according to the

$$\underset{\text{Sugar of milk.}}{C_{12}H_{12}O_{12}} = \underset{\text{Lactic acid.}}{2(HO.C_6H_5O_5)}.$$

The caseine, being insoluble in the acid fluid, separates in t curd. This development of lactic acid is spoken of as the *lacti tion*, and may be excited not only in milk sugar, but in other analogous to it. This is taken advantage of in the preparatic acid, for which purpose 8 parts of cane-sugar are dissolved in water, and 1 part of poor cheese with 3 parts of chalk are ad mixture, which is then allowed to remain for some weeks at al The lactic acid formed from the cane-sugar ($C_{12}H_{11}O_{11}$), under th of the changing caseine in the cheese, combines with the lime of disengaging the carbonic acid, and forming crystals of lacta ($CaO.C_6H_5O_5$). This is dissolved in boiling water, recrystallis

it, and digested with one-third of its weight of sulphuric acid, nverts the lime into sulphate, liberating the lactic acid; by add- hol, the whole of the sulphate of lime is precipitated, and the id is dissolved by the alcohol, which leaves it on evaporation as a s, syrupy, very acid liquid, which may be distilled, though with s from decomposition, if heated out of contact with air.

ating lactic acid to about 270° F. for a considerable length of equivalent of water is expelled from it, and the lactic anhydride) is left as a brownish glassy substance, which is reconverted into ated acid by boiling with water. At a temperature of 500° F. id undergoes a destructive distillation, the most interesting pro- which is a transparent crystalline substance called lactide ($C_6H_4O_4$), from lactic acid by the elements of two equivalents of water, resumes when dissolved in that liquid, being converted into lactic acid ($C_6H_6O_6$). When lactic acid is heated with hydriodic sealed tube, it is converted into propionic acid—

$$\underset{\text{tic acid.}}{C_6H_5O_5} + 2HI = \underset{\text{Propionic acid.}}{HO.C_6H_5O_5} + 2HO + I_2.$$

acid is an important constituent of the animal body, being found ice of muscular flesh, in the gastric juice, &c.

k be maintained at a temperature of about 90° F., the fermenta- iced by the caseine results in the production of alcohol and car- d, for although milk-sugar is not fermented like ordinary sugar ct with yeast, it appears, under the influence of the changing t a favourable temperature, to be converted first into grape-sugar and afterwards into alcohol and carbonic acid. The Tartars pre- ntoxicating liquid, which they call *koumiss*, by the fermentation

an acid is added to milk, the caseine is separated in the form of consequence of the neutralisation of the soda which retains it in fresh milk, and this curd carries with it, mechanically, the les of the milk, leaving a clear yellow *whey*.

preparation of cheese, the milk is coagulated by means of *rennet*, prepared from the lining membrane of a calf's stomach. This is ntact with the warm milk for some hours, until the coagulation is d. This action of rennet upon milk has not yet received any satis- xplanation. The curd is collected and pressed into cheeses, which ed to ripen in a cool place, where they are occasionally sprinkled . The peculiar flavour which the cheese thus acquires is due to nposition of the fatty matter under the influence of the caseine, se to the production of certain volatile acids, such as butyric, , and caproic, which have very powerful and characteristic odours. pening be allowed to proceed very far, ammonia is developed by faction of the caseine, and in some cases the above- d acids are produced, at the expense probably sugar of in the cheese, conferring the peculiar aroma some of it.

ifferent kinds of cheese dependent upon milk their preparation, the cheeses being obtained k containing a large portion of cream; at a heat, and makes good contains ter never fuses complete other.

Caseine.—The pure curd of milk is known as caseine, and essentially of carbon, hydrogen, nitrogen, oxygen, and a small (one per cent.) of sulphur. The simplest expression of the re analysis of caseine, in formula, would be $C_{144}H_{114}N_{18}O_{45}S$, but t lous complexity of this formula conveys a suspicion that the com pure caseine has yet to be fixed. By whatever process it has be hitherto it has always been found to retain saline matters. plexity of its composition accounts for its liability to undergo p decomposition.

Coagulated caseine is characterised by the facility with whic solved by alkaline solutions, such as carbonate of soda, yieldi upon the surface of which, when boiled, an insoluble pellicle for similar to that which forms upon the surface of boiled milk. caseine may also be dissolved by acetic or oxalic acid, but the sulphuric or hydrochloric acid reprecipitates it, these acids forming insoluble compounds with caseine.

If skimmed milk be carefully evaporated to dryness, and the f from the residue by ether, the caseine is left in the soluble f with milk-sugar, and is capable of dissolving in water or in w

Caseine appears to possess the properties of a weak aci combines both with the alkalies and alkaline earths, and is e be capable of partially neutralising the former. A mixture of slaked lime is sometimes used as a cement for earthenware, combining with the lime to form a hard insoluble mass. milk, washed and dried, is used by calico-printers, under t *lactarine*, for fixing colours. If it be dissolved in weak amm with one of the aniline dyes, printed on calico, and st ammonia is expelled, and the colour is left behind as an ins pound with the caseine.

Caseine, or a substance so closely resembling it as to be founded with it, is found in peas, beans, and most leguminou dried peas be crushed and digested for some time in tepid wat liquid is obtained, holding starch in suspension. If this be settle, the clear liquid is an impure aqueous solution of *legum* table caseine, which constitutes about one-fourth of the weight

This solution is not coagulated by heat, but becomes cov pellicle similar to that which forms upon the surface of boile is coagulated by acetic acid and by rennet, just as is the ca caseine of milk.

Sugar of milk.—When whey is evaporated to a small bulk to cool, it deposits hard white prismatic crystals of sugar lactine ($C_{12}H_{12}O_{12}$), which is much less soluble, and therefor than cane-sugar.

Like this latter it may be converted into grape-sugar (C taking up the elements of two equivalents of water when dilute acids. Milk-sugar resembles the other sugars [illegible] combining with some bases, such as the alkalies, alk[illegible] of lead; with the latter it forms two insoluble c

$$C_{24}H_{19}O_{19}, 5PbO \text{ and } C_{24}H_{19}O_{19}.$$

At about 300° F. the crystals of milk-sugar equivalents of water, so that it does not appear formula should be written $C_{24}H_{19}O_{19}.5HO$.

will be seen that the characteristic constituents of milk are the
and milk-sugar, but the proportions in which these are present
idely, not only with the animal from which the milk is obtained,
th the food and condition of the animal. A general notion of their
e quantities, however, may be gathered from the following table,
ting the results of the analyses made by Boussingault :—

	Cow.	Ass.	Goat.	Woman.
Water, . . .	87·4	90·5	82·0	88·4
Butter, . . .	4·0	1·4	4·5	2·5
Milk-sugar, Soluble salts,	5·0	6·4	4·5	4·6
Caseine, Insoluble salts,	3·6	1·7	9·0	3·8

e soluble salts present in milk include the phosphates of potash and
and the chlorides of potassium and sodium, whilst the insoluble
are the phosphates of lime, magnesia, and oxide of iron. All these
are in great request for the nourishment of the animal frame.
e milk supplied to consumers living in towns is subject to consider-
adulteration; but in most cases this is effected by simply removing
eam and diluting the skimmed milk with water, a fraud which is
asily detected, as might be supposed, by determining the specific
ty of the milk, for since milk is heavier than water (1·032 sp. gr.),
the fatty matter composing cream is lighter than water, a certain
tity of cream might be removed, and water added, without altering
pecific gravity of the milk.
e most satisfactory method of ascertaining the quality of the milk
rs to consist in setting it aside for twenty-four hours in a tall narrow
(*lactometer*), divided into 100 equal parts, and measuring the pro-
n of cream which separates, this averaging, in pure milk, from eleven
rteen divisions. By shaking milk with a little potash (to dissolve
embrane which envelopes the fat globules) and ether, the butter may
solved in the ether which rises to the surface, and if this be poured
d allowed to evaporate, the weight of the butter may be ascertained.
grains of milk should give, at least, 27 or 28 grains of butter.
, however, the milk of the same cow gives very different quantities
am at different times, it is difficult to state confidently that adultera-
as been practised. It is said that certain yellow colouring matters,
as annatto and turmeric, as well as gum, starch, &c., are occasionally
yed to confer an appearance of richness upon impoverished milk.

4. Blood.—The blood [illegible] the various organs of the body
ly receive their nour[illegible] most important, as well as the
complex of the anima[illegible] chemical examination is attended
much difficulty, on [illegible] rapidity with which it changes
[illegible]
[illegible] fresh[illegible] the microscope, it is observed
[illegible] its physical constitution, consist-
[illegible] in a transparent liquid; the
[illegible] ll marked red colour.

In a few minutes after the blood has been drawn, it begins to assume a gelatinous appearance, and the semi-solid mass thus formed separates into a red solid portion or *clot*, which continues to shrink for ten or twelve hours, and a clear yellow liquid or *serum*. It might be supposed that this coagulation is due to the cooling of the blood, but it is found by experiment to take place even more rapidly when the temperature of the blood is raised one or two degrees after it has been drawn; and on the other hand, if it be artificially cooled, its coagulation is retarded. Indeed the reason for this remarkable behaviour of the blood is not yet understood.

If the coagulum or clot of blood be cut into slices, tied in a cloth, and well washed in a stream of water, the latter runs off with a bright red colour, and a tough yellow filamentous substance is left upon the cloth; this substance is called *fibrine*, and its presence is the proximate cause of the coagulation of the blood, for if the fresh blood be well whipped with a bundle of twigs or glass rods, the fibrine will adhere to them in yellow strings, and the *defibrinated* blood will no longer coagulate on standing. If this blood, from which the fibrine has been extracted, be mixed with a large quantity of a saline solution (for example, 8 times its bulk of a saturated solution of sulphate of soda), and allowed to stand, the red globules subside to the bottom of the vessel.

These globules are minute bags of red fluid, enclosed in a very thin membrane or *cell-wall*, and if water were mixed with the defibrinated blood, since its specific gravity is lower than that of the fluid in the globules, it would pass through the membrane (by *endosmose*), and so swell the latter as to break it and disperse the contents through the liquid.

The red fluid contained in these blood globules consists of an aqueous solution, containing as its principal constituents a substance known as *globuline*, which very nearly resembles albumen, and the peculiar colouring matter of the blood, which is called *hæmatine*.

Beside these, the globules contain a little fatty matter and certain mineral constituents, especially the iron (which is associated in some unknown form with the colouring matter), the chlorides of sodium and potassium, and the phosphates of potash, soda, lime, and magnesia.

Though the quantities of these constituents are not invariable, even in the same individual, the following numbers may be taken as representing the average composition of these globules:—

1000 *parts of Blood Globules contain*—

Water,	688·00	Organic substances of unknown nature,	2·60
Globuline,	282·22		
Hæmatine,	16·75	Mineral substances,*	8·12
Fat,	2·31		

The mineral substances consist of—

Potassium,	8·328	Oxygen,	0·667
Phosphoric acid,	1·184	Phosphate of lime,	0·114
Sodium,	1·052	Phosphate of magnesia,	0·073
Chlorine,	1·686	Sulphuric acid,	0·066

Globuline is a substance very similar in its character and composition to albumen; it is found also in large proportion in the matter composing the crystalline lens of the eye.

The *hæmatine* or *hæmatosine* must be accounted the most important

* Exclusive of the iron which is associated with the hæmatine.

tituent of the blood globules, since it appears to be more intimately
ected than any other with the functions discharged by the blood in
ition and respiration.

order to obtain it in the separate state, the blood globules are boiled
alcohol acidulated with sulphuric acid, and the red solution mixed
carbonate of ammonia, which separates the greater part of the globu-
the filtered liquid is evaporated to dryness, and all soluble matters
xtracted by successive treatments with water, alcohol, and ether. By
dissolving the brown residue in alcohol containing ammonia, filter-
evaporating to dryness, and removing any soluble matter by water, a
brown substance is obtained, which is supposed to be pure hæmatine,
gh no longer in the soluble state in which it existed in the blood. It
ow dissolved only by alkalies or by acidulated alcohol.

n its chemical composition hæmatine is remarkable for the presence
ron, associated in a very intimate manner with carbon, hydrogen,
ogen, and oxygen, so that it cannot be recognised by the ordinary
s. The formula which has been assigned to it is $C_{68}H_{36}N_8O_{12}Fe$, but it
ather doubtful whether it has been analysed in a perfectly pure state.

The most important chemical property of hæmatine is its behaviour
th oxygen. It is well known that the blood issuing from an artery has
much brighter red colour than that drawn from a vein, and that when
e latter is allowed to coagulate, the upper part of the clot, which is in
ntact with the air, is brighter than the lower part.

When the dark red blood drawn from a vein is shaken up with air or
xygen, a quantity of the latter is absorbed, and a nearly equal volume of
rbonic acid is disengaged, the dark red colour being at the same time
hanged to the bright red characteristic of arterial blood. The carbonic
id exists already formed in the venous blood, and is given off if the
lood is exposed under an exhausted receiver. The condition assumed
y the oxygen when absorbed by the blood is not yet clearly understood,
ut it is generally allowed that the conversion of venous into arterial
lood is due to the displacement of carbonic acid by oxygen.

The liquid in which the blood globules float is an alkaline solution con-
ining albumen, fibrine, and saline matters in about the proportions here
dicated.

1000 *parts of* Liquor Sanguinis *contain*—

Water,	902·90	Organic substances of unknown nature,	8·94
Albumen,	78·84		
Fibrine,	4·05	Mineral substances,	8·55
Fat,	1·72		

The mineral substances consist of—

Sodium,	3·341	Phosphoric acid,	
Chlorine,	3·644	Sulphuric acid,	
Potassium,	0·323	Phosphate of lime,	
Oxygen,	0·403	Phosphate of magnesia	

The alkaline character of this liquid a due t
arbonate and phosphate of soda.

The *albumen* present in the serum
elatinous mass when heated, this pr
f albumen. This substance may be

mass, resembling gum, and dissolving slowly in water, by eva either serum of blood or white of egg below 120° F.; but if the t ture be raised above that point, the albumen is coagulated, and ca redissolved in water unless heated with it under pressure.

Albumen, like caseine, has never been obtained perfectly fr saline matters, particularly the alkaline and earthy phosphates, an difficulty attends the exact determination of its composition. The formula which can be assigned to it is $C_{288}H_{240}N_{36}O_{80}S_2$.

It will be remembered that a substance identical with, or very resembling, albumen, and known as *vegetable albumen*, is found vegetable juices which are coagulated by heat.

Fibrine, as existing in blood, differs from all other animal su by its tendency to spontaneous coagulation. When coagulated it characters very similar to those of coagulated albumen; but wh rated from the freshly drawn blood by violent stirring, it form strings which dry into a yellow horny mass. Fibrine is one of t important constituents of the animal frame, for all muscular flesh of this substance. The gluten found in the seeds of the cereals very close resemblance to fibrine, and is often called *vegetable fib*

The same formula has been often assigned to fibrine as to albu its complexity would explain its disposition to putrefy when from the influence of life. It does not appear quite certain fibrine dissolved in the blood is identical in composition with muscular fibre. Some analyses have shown that the muscular fi tains more oxygen than blood-fibrine, and this latter more than affording some ground for the belief that the blood-fibrine repr transition state between the albumen of the serum and the mus into which it is eventually converted.

Albumen, fibrine, and caseine have been regarded by some as compounds of the same primary substance (*proteine*) comb different proportions of sulphur and phosphorus, the prote isolated by boiling the albuminous body with potash and precip solution by an acid. The composition usually assigned to this is $C_{36}H_{27}N_4O_{12}$; but since it is neither crystallisable nor capable sion into vapour, there is no proof of its purity; and the great has been made of this substance by writers on animal chemistry the apparent simplicity which it confers upon the relation between the numerous modifications of albumen, fibrine, and c ultimate formulæ of which present so high a degree of complexi

—Eggs.—The shell of the egg contains about nine-tenths of its carbonate of lime, associated with animal matter. The white o sists of albumen (about 12 per cent.), water (about 86 per c small quantities of soluble salts. It is alkaline, from the pre little soda. Raw white of egg has no smell of sulphuretted and does not blacken silver; but after boiling, both these pro manifested, showing that it suffers some decomposition during co

Yolk of egg contains a modification of albumen termed *vite* owes its colour to a yellow oil which may be extracted with contains phosphoric acid. The yolk of hens' eggs has about weight of the white, and commonly contains about half its water, 16 per cent. of vitelline, 30 per cent. of fat, and 1·5 p aline matters.

5. FLESH.—The fibrine composing muscular flesh contains about
-fourths of its weight of water, a part of which is due to the blood
ined in the vessels traversing it, and another part to the *juice of flesh*,
h may be squeezed out of the chopped flesh. In this juice of flesh
are certain substances which appear to play a very important part in
ition. The liquid is distinctly acid, which is remarkable when the
line character of the blood is considered, and contains phosphoric,
c, and butyric acid, together with kreatine, inosite, and saline matters.
oaking minced flesh in cold water and well squeezing it in a cloth, a
fluid is obtained containing the juice of flesh mixed with a little
d. When the liquid is gently heated, the albumen of the blood and
he juice is coagulated in flakes stained with the colouring matter;
liquid filtered from these may be mixed with baryta water to precipi-
the phosphoric acid; and after a second filtration, evaporated to a
py consistence and set aside, when beautiful colourless prismatic
als are obtained, consisting of a feeble organic base called *kreatine*,*
omposition of which is represented by the formula $C_8H_9N_3O_4 . 2Aq.$
ie quantity of this substance obtained from the flesh of different
als varies very considerably, that of fowls having been found hitherto
productive, and next that of fish. 1000 parts of the flesh of fowl
shed 3·2 parts of kreatine, 1000 parts of cod, 1·71 of kreatine, and
of beef, 0·70 parts. Human flesh is said to contain a large proportion
eatine.

hen boiled with acids, kreatine loses the elements of water, and is
erted into a powerful base called *kreatinine* ($C_8H_7N_3O_2$), which is also
l in minute proportion, accompanied by kreatine, in the urine.

iled with alkalies, kreatine gains the elements of water, and furnishes
organic bases, *urea* (also found in urine), and *sarcosine* (σάρξ, flesh).

$$\underset{\text{Kreatine.}}{C_8H_9N_3O_4} + 2HO = \underset{\text{Urea.}}{C_2H_4N_2O_2} + \underset{\text{Sarcosine.}}{C_6H_7NO_4}.$$

the concentrated flesh-extract which has deposited the kreatine,
may be obtained, by careful treatment, crystals of a sweet substance
l *inosite* or *sugar of flesh*, and having the composition $C_{12}H_{12}O_{12} . 4Aq.$
temperature below 212° F. it loses two equivalents of water, and has
the same composition as dry grape-sugar, $C_{12}H_{14}O_{14}$, with which,
ever, it is certainly not identical.

osite has been obtained in very minute proportion from flesh, but
pe beans are said to yield as much as 0·75 per cent. of this interesting
r.

he saline constituents of the juice of flesh are chiefly phosphates of
sh, magnesia, and lime, with a little chloride of sodium.

is worthy of notice that potash is the predominant alkali in the
of flesh, whilst soda predominates in the blood, especially in the
m.

cording to Liebig, the acidity of the juice of flesh is chiefly due to
acid phosphate of potash, $KO . 2HO . PO_5$, whilst the alkalinity of
blood is caused by the phosphate of soda, $2NaO . HO . PO_5$; and it
been suggested that the electric currents which have been traced
muscular fibres are due to the mutual action between the acid ju
and the alkaline blood, separated only by thin membranes fr
r, and from the substance of the muscle and nerves.

* From κρέας.

The average composition of flesh may be represented as follows

Water, ...	78
Fibrine, vessels, nerves, cells, &c., ...	17
Albumen, ...	2·5
Other constituents of the juice of flesh, . .	2·5
	100·0

Cooking of Meat.—A knowledge of the composition of the juice explains the practice adopted in boiling meat, of immersing it at boiling water, instead of placing it in cold water, which is aft raised to the boiling point. In the latter case, the water would a the meat, and remove the important nutritive matter contained juice; whilst, in the former, the albumen in the external layer of at once coagulated, and the water is prevented from penetrating interior. In making soup, of course, the opposite method should lowed, the meat being placed in cold water, the temperature of t gradually raised, so that all the juice of flesh may be extracted, muscular fibre and vessels alone left.

The object to be attained in the preparation of beef-tea, is the ex of the whole of the soluble matters from the flesh, to effect wh meat should be minced as finely as possible, soaked for a short tin equal weight of cold water, and slowly raised to the boiling p which it is maintained for a few minutes. The liquid strained f residual fibrine contains all the constituents of the juice exc albumen, which has been coagulated.

When meat is roasted, the internal portions do not generally sufficiently high temperature to coagulate the albumen of the ju the outside is heated far above 212° F.; so that the meat impregnated to a greater extent with the melted fat, and some of stituents of the juice in this part suffer a change, which gives ris peculiar flavour of roast meat. The brown sapid substance t duced has been called *osmazome*,* but nothing is really known of nature.

In salting meat for the purpose of preserving it, a great dea juice of flesh oozes out, and a proportionate loss of nutritive matt tained.

446. *Gelatine.*—When portions of meat, containing cartilages or tendons, are boiled for some time with water, the liquid so sets to a jelly on cooling. This is due to the presence of *ge chondrine*, or both—substances so nearly resembling each other, were long confounded under the name of gelatine. The differenc origin is that gelatine is obtained by the action of water at a h perature on skin, membrane, and bone,† whilst chondrine is obt the same way from the cartilages. In their properties there is v difference, the most important being that a solution of chondrine pitated by acetic acid, by alum, and by acetate of lead, which do cipitate gelatine.

In composition there is a considerable difference between gela

* From οσμή, odour; ζωμός, soup.

† The animal matter of bone appears to be isomeric with gelatine, and is ca

ndrine, the latter containing considerably more oxygen and less nitro-
. The simplest formulæ which have been assigned to them are—

Gelatine, . . .	$C_{82}H_{67}N_{13}O_{32}$
Chondrine, . . .	$C_{72}H_{9}N_{9}O_{32}$

; they both contain phosphates of lime and magnesia in a very intimate
te of association.

The characteristic properties of gelatine are the tendency of its solution
gelatinise on cooling, and the formation of an insoluble compound with
nnic acid. The latter is the foundation of the art of tanning (p. 591),
d the former is turned to account in the preparation of jelly, size, and
ue. A solution containing only one per cent. of gelatine will set on
oling, though if it be repeatedly boiled it loses this property.

Isinglass is a very pure variety of gelatine prepared from the air bladder
fishes, especially of the sturgeon.

For the manufacture of *glue* the refuse and parings of hides are gene-
lly employed, after being cleansed from the hair and blood by steeping
lime water, and thoroughly exposed to the air for some days, so as to
nvert the lime into carbonate, and prevent the injurious effect of its
kaline character upon the gelatine. They are then boiled with water
ll the solution is found to gelatinise firmly on cooling, when it is run
f into another vessel, where it is kept warm to allow the impurities to
ttle down, after which it is allowed to gelatinise in shallow wooden
olers. The jelly is cut up into slices, and dried upon nets hung up in
free current of air. Spring and autumn are usually selected for drying
ue, since the summer heat would liquefy it, and frost would, of course,
lit it, and render it unfit for the market.

Size is made in a similar manner, but finer skins are employed, and
e drying is omitted, the size being used in the gelatinous state. The
st size is made from parchment cuttings.

By the action of acids or alkalies upon gelatine, two crystalline organic
ses may be obtained, known by the names of *glycocoll*, *glycocine*, or
gar of gelatine ($C_4H_5NO_4$), and *leucine* ($C_{12}H_{13}NO_4$).

It will be seen that glycocine is isomeric with nitrous ether ($C_4H_5O.NO_3$),
d leucine with the (at present unknown) nitrous ether of the caproic
ies. Leucine has been found in bullock's lungs and in calf's liver.

A large number of animal substances very nearly resemble gelatine in
eir composition; among these are hair, wool, nails, horns, and hoofs.

Hair contains, in addition to carbon, hydrogen, nitrogen, and oxygen,
m 3 to 5 per cent. of sulphur.

Wool has sometimes to be separated from the cotton in worn-out mixed
rics. The mixture is plunged into diluted hydrochloric acid, dried at
0° F., and submitted to the action of a machine (*devil*), which removes
e cotton, rendered brittle by the action of the acid, in the form of dust,
d leaves the wool fibres untouched. When the object is to save the
tton fibre, the fabric is exposed to high-pressure steam, which has no
ion upon cotton, but converts the wool into a brown matter easily re-
oved by a beating machine, and sold, for manure, as *ulmate of am-
mia*.

Silk is said to consist of three layers, the outermost consisting of gela-
e, and soluble in water; the next of albumen, soluble in acetic acid on
iling; and the third of a nitrogenised substance called *sericine*, which is

insoluble in water and acetic acid. Spider's threads appear to consist of this substance.

Sponge consists of a similar material, which has been called *fibroine*.

447. URINE.—The urine of animals is characterised by the presence of certain substances which are only met with in very minute quantities, if at all, in a state of health, in the other fluids of the body. The most important of these are an organic base called *urea*, *uric acid*, and *hippuric acid*.

Urea.—When human urine is evaporated to about an eighth of its original bulk, and mixed with an equal volume of nitric acid, a semi-solid mass is formed consisting of pearly scales of nitrate of urea ($C_2H_4N_2O_2 . HO . NO_5$). If these be washed with cold water, afterwards dissolved in boiling water, and treated with carbonate of baryta, the nitric acid combines with the baryta, and the carbonic acid having no tendency to combine with the urea, passes off, leaving the urea in solution—

$$\underset{\text{Nitrate of urea.}}{C_2H_4N_2O_2 . HO . NO_5} + BaO . CO_2 = \underset{\text{Urea.}}{C_2H_4N_2O_2} + BaO . NO_5 + HO + CO_2.$$

After filtering from the excess of carbonate of baryta, the liquid is evaporated on a water-bath, when a mixture of urea and nitrate of baryta is obtained, from which the urea may be extracted by hot alcohol. On evaporating the alcohol, beautiful prismatic crystals of urea are deposited. These crystals, when once separated from the urine in a pure state, may be preserved indefinitely even if dissolved in water; but the urea occurring in the urine is very soon decomposed, a putrefactive decomposition being excited by the *mucus*, a changeable substance somewhat resembling albumen, which collects in feathery clouds in the urine. The change which is thus induced in the urea results in its conversion into carbonate of ammonia—

$$\underset{\text{Urea.}}{C_2H_4N_2O_2} + 4HO = \underset{\text{Carbonate of ammonia.}}{2(NH_4O . CO_2)} .$$

It is in consequence of this change that the urine so soon exhales an ammoniacal odour. In order to effect the same change in pure urea, it is necessary to heat it with water under high pressure. When urea is combined with hydrochloric acid, and the hydrochlorate is heated, it furnishes hydrochlorate of ammonia and cyanuric acid, according to the equation—

$$\underset{\text{Hydrochlorate of urea.}}{3(C_2H_4N_2O_2 . HCl)} = 3(NH_3 . HCl) + \underset{\text{Cyanuric acid.}}{3HO . C_6N_3O_3} .$$

When cyanuric acid is distilled, it yields 3 equivalents of hydrated cyanic acid ($HO . C_2NO$), and the connexion thus established between urea and the cyanogen series becomes intelligible when we see that this base is isomeric with cyanate of ammonia ($NH_3 . HO . C_2NO$). In fact, by combining hydrated cyanic acid with ammonia, and evaporating the solution, no cyanate of ammonia, but simply urea, is obtained.

Upon this has been founded a process for obtaining urea artificially, which has attracted a great deal of attention as one of the earliest examples of the production in the laboratory, of a complex substance formed in the animal body. For the artificial production of urea, 56 parts of well-dried ferrocyanide of potassium are intimately mixed with 28 parts of dried binoxide of manganese, and the mixture heated to dull redness in an iron

, and stirred until it ceases to smoulder. The oxygen supplied by the oxide of manganese converts the potassium and part of the cyanogen he ferrocyanide into cyanate of potash, the remainder of the cyanogen ig burnt, and the iron converted into oxide—

$$\underset{\text{Ferrocyanide of potassium.}}{K_2(C_2N)_2Fe} + O_2 = \underset{\text{Cyanate of potash.}}{2(KO.C_2NO)} + 2CO_2 + N + FeO.$$

n treating the residue with cold water, the cyanate of potash is dis- ed out, and after the insoluble portion has subsided, the liquid may oured off, and 41 parts of sulphate of ammonia dissolved in it. Sul- te of potash and cyanate of ammonia are thus formed—

$$O.C_2NO + NH_3.HO.SO_3 = KO.SO_3 + NH_3.HO.C_2NO$$

if the solution be evaporated to dryness (on a water-bath) the latter is transformed into urea, which may be separated from the sulphate otash by alcohol, which dissolves the urea only.

48. The true constitution of urea has been the subject of much discussion among mists. The circumstance that, under certain conditions, this base assimilates elements of four equivalents of water and is converted into carbonate of ammonia, led to the opinion that urea should be classed among the amides (p. 549), when ould be represented as derived from two equivalents of carbonate of ammonia $(H_4O.CO_2)$ by the loss of four equivalents of water, just as oxamide is derived a oxalate of ammonia—

$$\underset{\text{Carbonate of ammonia.}}{2(NH_4O.CO_2)} - 4HO = \underset{\text{Urea.}}{C_2H_4N_2O_2}$$

$$\underset{\text{Oxalate of ammonia.}}{2(NH_4O.C_2O_3)} - 4HO = \underset{\text{Oxamide.}}{2(C_2H_2NO_2)}.$$

he question naturally presents itself, whether the various bases formed by sub- ution from ammonia (p. 539) would furnish corresponding ureas when acted n by cyanic acid. This has been actually found to be the case; ethylamine $_2(C_4H_5)$, for example, acting upon cyanic acid, yields ethyl-urea, which is isomeric h the cyanate of ethylamine, just as urea is isomeric with cyanate of ammonia.

$$\underset{\text{Cyanate of ethylamine.}}{NH_2(C_4H_5)HO.C_2NO} = \underset{\text{Ethyl-urea.}}{C_2H_3(C_4H_5)N_2O_2}.$$

t is evident that if urea be derived from a double molecule of ammonia by the stitution of C_2O_2 for H_2, then ethyl-urea will be derived in a similar manner a a double molecule of ethylamine.

$$\underset{\text{Ethylamine.}}{N_2H_4(C_4H_5)_2} \qquad \underset{\text{Ethyl-urea.}}{N_2H_3(C_4H_5)(C_2O_2)''}.$$

his case it will be observed that the diatomic group, C_2O_2, is substituted for one n of the hydrogen, and one atom of its representative, ethyle.

t will be remembered that the amides can be obtained by the action of ammonia n the corresponding ethers; thus oxalic ether treated with ammonia gives oxamide, the conversion may be intelligibly represented thus—

$$\underset{\text{Oxalic ether.}}{\left.\begin{matrix}(C_4O_4)''\\(C_4H_5)_2\end{matrix}\right\}O_4} + \underset{\text{Ammonia.}}{\left.\begin{matrix}H_2\\H_2\\H_2\end{matrix}\right\}N_2} = \underset{\text{Oxamide.}}{\left.\begin{matrix}(C_4O_4)''\\H_2\\H_2\end{matrix}\right\}N_2} + \underset{\text{Alcohol.}}{\left.\begin{matrix}H_2\\(C_4H_5)_2\end{matrix}\right\}O_4}.$$

n a similar manner, carbonic ether, when heated in a sealed tube with an holic solution of ammonia, yields urea and alcohol—

$$\underset{\text{Carbonic ether.}}{\left.\begin{matrix}(C_2O_2)''\\(C_4H_5)_2\end{matrix}\right\}O_4} + \underset{\text{Ammonia.}}{\left.\begin{matrix}H_2\\H_2\\H_2\end{matrix}\right\}N_2} = \underset{\text{Urea.}}{\left.\begin{matrix}(C_2O_2)''\\H_2\\H_2\end{matrix}\right\}N_2} + \underset{\text{Alcohol.}}{\left.\begin{matrix}H_2\\(C_4H_5)_2\end{matrix}\right\}O_4}.$$

When cyanic ether ($C_4H_5O \cdot C_2NO$) is acted on by ammonia, it yields ethyl-urea, the action being precisely parallel to that of ammonia upon cyanic acid—

$$\underset{\text{Cyanic acid.}}{HO \cdot C_2NO} + NH_3 = \underset{\text{Urea.}}{NH_2 \cdot HO \cdot C_2NO}$$

$$\underset{\text{Cyanic ether.}}{(C_4H_5)O \cdot C_2NO} + NH_3 = \underset{\text{Ethyl-urea.}}{NH_2 \cdot (C_4H_5)O \cdot C_2NO}.$$

Many other compound ureas of this description have been obtained, in which the hydrogen is partly or entirely replaced by the alcohol-radicals. The relation existing between these and their prototype, urea, will be seen in the following examples:—

Urea, ... $C_2H_4N_2O_2$

Ethyl-methyl-urea, . . $C_2\left\{\begin{matrix}C_4H_5\\C_2H_3\\H_2\end{matrix}\right\}N_2O_2$

Tetrethyl-urea, . . . $C_2(C_4H_5)_4N_2O_2$

Diphenyl-urea, . . . $C_2\left\{\begin{matrix}(C_{12}H_5)_2\\H_2\end{matrix}\right\}N_2O_2$.

The supposition that urea is really constituted upon the ammonia type derives some confirmation from the circumstance, that a number of substances have been obtained which bear the same relation to urea as the amides do to ammonia. They are, therefore, sometimes styled *ureides*, and sometimes compound ureas, in which a negative or acid radical occupies the place of a part of the hydrogen. In illustration of the mode of formation of the bodies of this class, the production of benzamide or benzoyl-urea may be referred to.

When ammonia acts upon chloride of benzoyle, it yields benzamide and hydrochloric acid—

$$\underset{\text{Chloride of benzoyle.}}{C_{14}H_5O_2 \cdot Cl} + NH_3 = \underset{\text{Benzamide.}}{C_{14}H_5O_2 \cdot NH_2} + HCl.$$

If urea be substituted for the ammonia, benzureide and hydrochloric acid are formed—

$$\underset{\text{Chloride of benzoyle.}}{C_{14}H_5O_2 \cdot Cl} + \underset{\text{Urea.}}{C_2H_4N_2O_2} = \underset{\text{Benzureide.}}{C_{14}H_5O_2 \cdot C_2H_3N_2O_2} + HCl.$$

Both reactions become much more intelligible if urea and its derivatives be allowed to be composed upon the ammonia type—

$$\underset{\text{Ammonia.}}{NH_3} + \underset{\text{Chloride of benzoyle.}}{(C_{14}H_5O_2)Cl} = \underset{\text{Benzamide.}}{NH_2(C_{14}H_5O_2)} + HCl$$

$$\underset{\text{Urea.}}{N_2H_4(C_2O_2)''} + \underset{\text{Chloride of benzoyle.}}{(C_{14}H_5O_2)Cl} = N_2H_3(C_{14}H_5O_2)\,(C_2O_2)'' + HCl.$$

By similar processes there have been obtained—

Acetyl-urea, ... $N_2H_3(C_4H_3O_2)(C_2O_2)''$

Butyryl-urea, ... $N_2H_3(C_8H_7O_2)\,(C_2O_2)''$, &c.

449. *Uric acid.*—When human urine is acidified with hydrochloric acid and allowed to stand for some time, it deposits minute hard red grains, consisting of *uric acid* ($C_{10}H_4N_4O_6$) tinged with the urinary colouring matter. In urine the acid is present as urate of soda and urate of ammonia, which are often deposited from urine in slight derangements of the system, when they are present in excess, these salts being very much more soluble in warm water than in cold. Since uric acid and its salts are very common ingredients of calculi, this acid is sometimes called lithic acid (λίθος, a stone).

As the quantity of uric acid in human urine does not exceed 1 grain in 1000, recourse is had to other sources for the preparation of this acid.

which is now extensively used for the preparation of the *murexide* employed in calico-printing.

The excrements of the boa-constrictor and of birds, which consist almost entirely of acid urate of ammonia, and *guano*, which has been formed by the partial decomposition of the excrements of sea-birds, are excellent sources of uric acid. The separation of the uric acid from acid urate of ammonia is easily effected by dissolving it in solution of potash, filtering, and adding hydrochloric acid, when the uric acid, which requires 10,000 parts of cold water to dissolve it, is precipitated as a white crystalline powder.

When a solution of potash is saturated with uric acid in the cold, and boiled down out of contact with air, small needle-like crystals are deposited, having the composition $2KO . C_{10}H_2N_4O_4$, and if this be dissolved in water, and carbonic acid be passed through the solution, half the potash is removed as carbonate, and a granular precipitate of acid urate of potash, $KO . HO . C_{10}H_2N_4O_4$, is deposited. Uric acid, therefore, is a bibasic acid, and the formula of the acid itself ($C_{10}H_4N_4O_6$) should be written $2HO . C_{10}H_2N_4O_4$.

When uric acid is added by degrees to strong nitric acid, it dissolves with effervescence and evolution of heat; the solution, on cooling, deposits octahedral crystals of a substance called *alloxan* ($C_8H_2N_2O_8$), which may be represented as formed by the oxidation of the uric acid according to the following equation—

$$\underset{\text{Uric acid.}}{C_{10}H_4N_4O_6} + HO . NO_5 = \underset{\text{Alloxan.}}{C_8H_2N_2O_8} + 2CO_2 + N_2 + NH_3 .$$

Alloxan has the curious property of staining the fingers of a beautiful pink colour, and its solution gives an intense purple colour with sulphate of iron.

A connexion is established, by means of alloxan, between uric acid and urea, which becomes important, because these two bodies, accompanied by a small quantity of alloxan, are always found together in the urine. Alloxan appears to be the intermediate stage in the conversion of uric acid into urea by oxidation, for if a solution of alloxan be boiled with peroxide of lead (PbO_2) carbonic acid is evolved, and the alloxan is converted into urea by oxidation—

$$\underset{\text{Alloxan.}}{C_8H_2N_2O_8} + 2HO + 4PbO_2 = \underset{\text{Urea.}}{C_2H_4N_2O_2} + 6CO_2 + 4PbO .$$

When sulphuretted hydrogen is passed through a solution of alloxan, the liquid is troubled by the separation of sulphur, and deposits prismatic crystals of *alloxantine* ($C_{16}H_4N_4O_{14}$), which is derived from two equivalents of alloxan by the removal of two equivalents of oxygen—

$$\underset{\text{Alloxan.}}{2C_8H_2N_2O_8} + 2HS = \underset{\text{Alloxantine.}}{C_{16}H_4N_4O_{14}} + 2HO + S_2 .$$

If 4 grains of alloxantine and 7 grains of crystallised alloxan be dissolved in half an ounce of hot water, and 80 grains of a cold saturated solution of carbonate of ammonia added, the carbonic acid is disengaged with effervescence, and the liquid assumes a brilliant purple colour, depositing as it cools splendid crystals, which have a red colour by transmitted light, and reflect a play of green and gold, like the wing of the sun-beetle.

This magnificent substance is known as *murexide*, and appears to be formed according to the following equation—

$$\underset{\text{Alloxantine.}}{C_{16}H_4N_4O_{14}} + \underset{\text{Alloxan.}}{C_8H_2N_2O_8} + 4NH_3 = \underset{\text{Murexide.}}{C_{24}H_{12}N_{10}O_{16}} + 6HO .$$

The beautiful colour of murexide has been applied in dyeing and calico-printing, being prepared for that purpose from the uric acid furnished by guano.

450. *Hippuric acid.*—Another acid peculiar to the urine, and found in very minute quantity in human urine, is hippuric acid ($C_{18}H_9NO_5$), so named because it occurs in far larger quantity in the urine of horses (ἵππος, *a horse*) and cows, the cow's urine yielding more than 1 per cent. of the acid. It is generally prepared from cow's urine by evaporating it to about an eighth of its bulk, and adding an excess of hydrochloric acid. On standing, long prismatic needles of hippuric acid are deposited. It is remarkable that this acid can be obtained only from the urine of stall-fed cows, or of horses kept at rest, for if the animals are actively exercised, the above treatment educes benzoic acid ($C_{14}H_6O_4$) in place of hippuric. Again, only the fresh urine yields hippuric acid, for after putrefaction, only benzoic acid can be obtained from it. Conversely, if benzoic acid be administered to an animal, it makes its appearance as hippuric acid in the urine.

The relation between these two acids becomes evident when hippuric acid is boiled for some time with strong hydrochloric acid; on cooling, the solution deposits crystals of benzoic acid, and if the liquid separated from these be evaporated, neutralised with ammonia and mixed with alcohol, crystals of glycocoll (p. 617) are obtained—

$$\underset{\text{Hippuric acid.}}{C_{18}H_9NO_5} + 2HO = \underset{\text{Benzoic acid.}}{C_{14}H_6O_4} + \underset{\text{Glycocoll.}}{C_4H_5NO_4}.$$

This result has been confirmed synthetically by acting upon the compound resulting from the action of glycocoll on oxide of zinc, with chloride of benzoyle (p. 475), when hippuric acid is reproduced.

$$\underset{\text{Zinc-glycocoll.}}{C_4(H_4Zn)NO_4} + \underset{\text{Chloride of benzoyle.}}{C_{14}H_5O_2.Cl} = ZnCl + \underset{\text{Hippuric acid.}}{C_{18}H_9NO_5}.$$

Hippuric acid, therefore, may be represented as *benzoyle-glycocoll*, $C_4H_4(C_{14}H_5O_2)NO_4$. A very interesting illustration of the doctrine of substitution is connected with these acids. By acting upon hippuric acid with nitric and sulphuric acids, it is converted into nitro-hippuric acid by the substitution of NO_4 for one equivalent of its hydrogen, and if this acid be boiled with hydrochloric acid, it yields nitrobenzoic acid, just as hippuric yields benzoic acid—

$$\underset{\text{Nitro-hippuric acid.}}{C_{18}\left\{\begin{matrix}H_8\\NO_4\end{matrix}\right\}NO_5} + 2HO = \underset{\text{Nitro-benzoic acid.}}{C_{14}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right\}O_4} + \underset{\text{Glycocoll.}}{C_4H_5NO_4}.$$

In contact with bases, hippuric acid forms salts of the general formula $MO.C_{18}H_8NO_5$, so that the acid itself should be written as $HO.C_{18}H_8NO_5$.

In addition to the organic substances which have been already mentioned as occurring in the urine (urea, uric acid, mucus, hippuric acid, kreatinine), it always contains a large proportion of alkaline and earthy salts, especially of chloride of sodium, phosphate and sulphate of potash, and phosphates of lime, magnesia, and ammonia.

verage composition of human urine may be thus stated—

Water,	956·80
Urea,	14·23
Uric acid,	0·37
Mucus,	0·16
Hippuric acid, kreatinine, colouring matter, and unknown organic matters,	15·03
Chloride of sodium,	7·22
Phosphoric acid,	2·12
Potash,	1·93
Sulphuric acid,	1·70
Lime,	0·21
Magnesia,	0·12
Soda,	0·05
	999·94

CHEMISTRY OF VEGETATION.

The ultimate elements of plants, that is, the substances with which must be supplied in one form or other, to sustain their growth, bon, hydrogen, nitrogen, oxygen, sulphur, phosphorus, chlorine, potassium, sodium, calcium, magnesium, iron, manganese.

hese, the carbon, hydrogen, nitrogen, oxygen, sulphur, and phos- are grouped together to form the various organic compounds ed by plants, the remaining elements being arranged generally in lowing forms :—

rides of potassium and sodium,

hate of lime,

ates of potash and soda,

sphates of iron (manganese?), lime, magnesia, and ammonia,

pounds of potash, soda, and lime, with vegetable acids.

ts are capable of receiving food either in the form of gas through strumentality of their leaves, or in solution by their roots.

carbon, which is their most important constituent as regards quantity, en up in the form of carbonic acid by both these organs of the This carbonic acid is derived either from the surrounding atmo- or from the decay of the organic matters contained in the soil surrounds the roots of the plant.

hydrogen is derived partly from water and partly from the am- which is carried down to the roots of the plant by rain, or is d in the putrefaction and decay of the nitrogenised organic matters soil. The ammonia also forms one great source of the nitrogen in , another being the nitric or nitrous acid, which is either brought by the rain, or formed within the soil by the nitrification of the nia (p. 122). As to the oxygen, it is obtained both from the car- acid and water, which contain this element in larger proportion than present in any vegetable product.

sulphur and phosphorus contained in the organic parts of the appear to be chiefly derived from the sulphates and phosphates of il.

chlorine, silicon, and the metals, are derived from the mineral con- ts of the soil.

s not difficult to imagine the course of formation of a fertile soil primary rock (of granite, for example) under the influence of the phere and rain, exerted through a very long period.

It will be remembered that granite consists essentially of quartz (silica), feldspar (silicate of alumina and potash or soda), and mica (silicates of alumina, iron, potash, and magnesia); in addition to these there may always be found in granite minute quantities of phosphate of lime, of sulphates, of chlorides, and of manganese.

By the disintegration of such a rock under the action of air and moisture (p. 286), a soil will be formed containing the various *mineral* substances required for the food of the plant. If now, upon the thin layer of soil thus formed over the face of the rock, some seeds of the lower orders of plants, the lichens, for instance, be deposited, they will grow and fructify, deriving their carbon, hydrogen, nitrogen, and oxygen from the air and rain, and their mineral constituents from the soil. The death of these lichens would add new elements of fertility to the soil, in the shape of the food which they had condensed from the air, and of the saline ingredients which had been converted within their organisations into forms better suited to sustain the higher orders of plants. Given, then, the seeds of a higher vegetation, a similar process may be supposed to take place, and at length animals would be attracted to the spot by the prospect of vegetable food, and by transporting to it elements which they had derived from other sources, would eventually confer upon it the highest fertility. The soil then coming under tillage, the crops raised upon it are consumed by animals and removed to a distance, so that the mineral food contained in the soil is by degrees exhausted, and unless it is restored the soil becomes barren.

To restore its fertility is the object of manuring, which consists in adding to the soil some substance which shall itself serve directly as food for the plant, or shall so modify, by chemical action, some material already present in the soil, as to convert it into a state in which the plant may take advantage of it.

As examples of substances which are added as direct food for plants, may be enumerated—

(1.) The ashes of peat, turf, coal, &c., which furnish the mineral substances originally obtained from the soil by the vegetables from which these materials were formed.

(2.) Gypsum, or sulphate of lime, and sulphate of magnesia, which appear to be valuable not only as sources of sulphur, calcium, and magnesium, but because they are capable of decomposing the carbonate of ammonia, which is either brought down by rain or evolved by putrefaction in the soil, and of converting it into sulphate of ammonia which is retained in the soil, whereas the carbonate, being a volatile salt, would be again exhaled into the air and lost to the plants.

(3.) Phosphate of lime, or bone-ash, which is most commonly converted into the soluble superphosphate of lime (p. 223) by treatment with sulphuric acid, before being employed as a manure.

(4.) Chloride of sodium, or common salt, serves as a source of sodium, for in contact with the carbonate of lime, which is found in all fertile soils, it is partly converted into carbonate of soda, which may in turn be converted into silicate of soda, or any other salt of that alkali necessary to the growth of the plant.

(5.) Nitrate of soda (Peruvian nitre) is held to be of great service in some cases, as yielding both soda and nitrogen in a form serviceable to the plant.

(6.) The silicates of potash and soda, which are especially useful to

rops which, like the cereals, contain a considerable proportion of silica n their stems; since, although that substance is contained in abundance n all soils, it is not available for the plant unless converted into a soluble tate by combination with an alkali.

(7.) Sulphate of ammonia (derived from the gas-works) is, of course, useful both for its sulphuric acid and ammonia.

(8.) Plants, or parts of plants, ploughed into a soil, would obviously rnish food for other plants by their gradual putrefaction and decay.

(9.) Bones, which furnish carbonic acid and ammonia by the putrefaction of their gelatinous matter, as well as a large supply of phosphate of ne.

(10.) Urine, yielding much carbonate of ammonia by the decomposition its urea and uric acid, and an abundance of the phosphates and other line matters required by the plant.

(11.) Solid excrements of various animals, containing the insoluble lts (especially phosphates) of the animal's food, as well as easily putrescible organic matters yielding much ammonia and sulphuretted hydrogen.

(12.) Guano, the dung of carnivorous sea-birds, which owes its very gh value partly to the large proportion of urate of ammonia and other trogenised organic substances which it contains, and partly to the presence of phosphates and salts of the alkalies.

(13.) Soot, which appears to act chiefly by virtue of the salts of mmonia derived from the destructive distillation of the coal.

The chief substance employed for acting chemically upon the constituents of the soil, so as to render them more serviceable to the plant, is lime, which modifies in a very important manner both the organic and mineral portions of the soil. Its action upon the former consists in promoting its decay, and the conversion of its elements into those forms, viz., carbonic cid, water, ammonia, and nitric acid, in which they may be of service to the plant. Upon the inorganic constituents of the soil lime acts by ssisting the decomposition of minerals, particularly of those which contain the alkalies (such as feldspar), and thus converting them into soluble rms.

In some cases fertility is restored to an apparently exhausted soil, without the addition of manure, by allowing it to lie fallow for a time, so that, nder the influence of the air and moisture, such chemical changes may ke place in it as will again replenish it with food available for the crops. is not even necessary in all cases that the soil should be altogether reased from cultivation; for even though it may refuse to feed any longer ne particular crop, it may furnish an excellent crop of a different escription, and, which is more remarkable, it may, after growing two or ree different crops, be found to have regained its power of nourishing ne very crop for which it was before exhausted. Experience of this has d to the adoption of the system of *rotation of crops*, by which a soil is ade to yield, for example, a crop of barley, and then successive crops of ass, beans, turnips, and barley again.

The possibility of this rotation is partly accounted for by the difference the mineral food removed from the soil by different crops; thus turnips quire much of the alkalies and lime; wheat, much alkali and silica; arley, much lime and silica; and clover, much lime, so that the soil hich had been exhausted for wheat, because it no longer contained ough soluble silica, might still yield sufficient alkali and lime to a crop *turnips, and when the* alkali was exhausted, might furnish enough lime

to a crop of clover, after which, in consequence of the chemical change allowed by lapse of time in the soil, more of the original minerals composing it might have been decomposed and rendered available for a fresh wheat crop.

Another explanation of the benefit of systems of rotation may be given in those cases in which the débris of the preceding crop are allowed to remain on the land. Some plants, extending their roots more deeply into the soil, avail themselves of mineral food which is beyond the reach of plants furnished with shorter roots, and when the refuse of the former plants is ploughed into the land, the surface is enriched with the food collected from the sub-soil.

Our knowledge of the chemical operations taking place in the plant and resulting in the elaboration of the great variety of vegetable products, is very slight indeed. We appear to have sufficient evidence that sugar and starch, for example, are constructed in the plant from carbonic acid and water, that gluten results from the mutual action of the same compounds, together with ammonia, or nitric acid, and certain sulphates and phosphates, but what the intermediate steps in this conversion may be we are not in a position even to hazard a guess.

All seeds contain starch, gluten, or some similar nitrogenised substance (legumine, for example), together with mineral matters, these being provided for the nourishment of the young plant until its organs are sufficiently developed to enable it to procure its own food from the air or from the soil.

During the process of germination the seed absorbs oxygen and evolves carbonic acid, and since the albuminous constituent is the most mutable substance present, it is probably this which undergoes oxidation, and excites the conversion of the insoluble starch into soluble sugar. At this stage the seed requires, as is well known, a fair supply of water, the elements of which are required for the conversion of the starch ($C_{12}H_{10}O_{10}$) into sugar ($C_{12}H_{12}O_{12}$); water is also required to dissolve the sugar as well as the altered albuminous matter and the mineral salts, in order to form the sap of the embryo plant. These constituents of the sap, directed by the mysterious vital energy in the seed, build up the root, which extends itself in search of nourishment down into the soil, and the leaves which discharge a similar function with respect to the air. As soon as the leaves are developed, the plant becomes able to decompose carbonic acid, water, and ammonia, to provide the organic components of its sap. Some part of these changes at least appears to take place in the leaves of the plant, from which, during the day-time, oxygen (together with a little nitrogen) is continually evolved. The leaves have been compared to the lungs of animals, the functions of which they reciprocate, for whilst, in the lungs of animals, an absorption of oxygen and an evolution of carbonic acid is observed, in the leaves of plants, it is the carbonic acid which is absorbed and oxygen is disengaged.

In the dark, plants exhale carbonic acid, but in much smaller quantity than they decompose in the light.

That oxygen must be evolved, if plants construct their carbonaceous compounds from carbonic acid and water, is obvious on reflecting that all these compounds contain less oxygen, in proportion to their carbon and hydrogen, than is contained in carbonic acid and water.

Thus, we may conceive the formation of all the compounds of value

and hydrogen, or of those elements with oxygen, which are met with in plants, by the concurrence, in various proportions, of carbonic acid and water, and the separation of the whole or a part of their oxygen.

To take an example; cellulose ($C_{12}H_{10}O_{10}$) would result from the coalition of 12 eqs. of carbonic acid and 10 eqs. of water, with separation of 24 eqs. of oxygen. Again, malic acid, $C_8H_6O_{10}$, would require 8 eqs. of carbonic acid and 6 eqs. of water, whilst 12 eqs. of oxygen would be set free.

It is equally easy to represent the formation of nitrogenised compounds from carbonic acid, water, and ammonia, with separation of oxygen, for the nitrogen in all such compounds is present in so small a number of equivalents, relatively to the carbon and hydrogen, that the amount of oxygen separated from the carbonic acid and water would always far more than suffice to convert the whole of the hydrogen of the ammonia into water, even if this hydrogen did not itself take part in the formation of the compound. Suppose, for instance, that the formation of quinine is to be accounted for—

$$40CO_2 + 18HO + 2NH_3 = \underset{\text{Quinine.}}{C_{40}H_{24}N_2O_4} + O_{94}.$$

If sulphur be a constituent of the vegetable compound to be formed, it is conceivable that the sulphuric acid derived from the sulphates present in the soil should co-operate with the carbonic acid, water, and ammonia.

If the composition of gluten be correctly represented by the formula $C_{216}H_{169}N_{27}O_{68}S_2$, the equation explaining its formation from the above constituents of the food of the plant would be written—

$$216CO_2 + 88HO + 27NH_3 + 2SO_3 = C_{216}H_{169}N_{27}O_{68}S_2 + O_{478}.$$

The chemical tendency of vegetables, therefore, is to reduce to a lower state of oxidation the substances presented in their food, whilst animals exhibit a reciprocal tendency to oxidise the materials on which they feed.

With respect to the last stage in the existence of the plant, the ripening of the fruit, we know a little more concerning the chemical changes which it involves.

Most fruits, in their unripe condition, contain cellulose, starch, and some one or more vegetable acids, such as malic, citric, tartaric, and tannic, the latter being almost invariably present, and causing the peculiar roughness and astringency of the unripe fruit. The *characteristic* constituent of unripe fruits, however, is *pectose*, a compound of carbon, hydrogen, and oxygen, the composition of which has not been exactly determined. Pectose is quite insoluble in water, but during the ripening of the fruit it undergoes a change induced by the vegetable acids, and is converted into *pectine* ($C_{64}H_{40}O_{66}$), which is capable of dissolving in water, and yields a viscous solution. As the maturation proceeds, the pectine itself is transformed into *pectic acid* ($C_{32}H_{22}O_{30}$), and *pectosic acid* ($C_{32}H_{22}O_{30}$), which are soluble in boiling water, yielding solutions which gelatinise on cooling. It is from the presence of these acids, therefore, that many ripe fruits are so easily convertible into jellies.

Whilst the fruit remains green, its relation to the atmosphere appears to be the same as that of the leaves, for it absorbs carbonic acid, and evolves oxygen; but when it fairly begins to ripen, oxygen is absorbed *from the air, and carbonic acid* is evolved, whilst the starch and cellulose

NUTRITION OF ANIMALS.

452. Between the chemistry of vegetable and that of animal life there this fundamental distinction, that the former is eminently constructive, d the latter destructive. The plant, supplied with compounds of the mplest kind—carbonic acid, water, and ammonia—constructs such com- ex substances as albumen and sugar; whilst the animal, incapable of iving sustenance from the simpler compounds, being fed with those of more complex character, converts them eventually, for the most part, o the very materials with which the constructive work of the plant mmenced. It is indeed true, that some of the substances deposited in animal frame, such as fibrine and gelatinous matter, rival in com- xity many of the products of vegetable life; but for the elaboration these substances, the animal must receive food somewhat approach- them in chemical composition. It is to this nearer resemblance ween the food of animals and the proximate constituents of their ues, that we may partly ascribe the greater extent of our knowledge the subject of the nutrition of animals, which is, however, far from g complete.

he *ultimate* elements contained in the animal body are the same as e of the vegetable, but the *proximate* constituents are far more erous and varied.

he bones, containing the phosphates and carbonates of lime and mag- , together with gelatinous matter, require that the animal should be lied with food which, like bread, contains abundance of phosphates, ell as the nitrogenised matter (gluten) from which the gelatinous tance may be formed. In milk, the food of the young animal, we also the necessary phosphates, whilst the caseine affords the supply itrogeneous matters.

uscular flesh finds, in the gluten of bread and the caseine of milk, the ogenised constituent from which its fibrine might be formed with even transformation than is required for the gelatinous matter of bone, e the composition of fibrine, gluten, and caseine is very similar.

he albumen and fibrine of the blood have also their counterparts in gluten and caseine of bread and milk, whilst all the salts of the blood be found in either of these articles of food.

Bread and milk, therefore, may be taken as excellent representatives he food necessary for animals, and the same constituents are received heir flesh diet by animals which are purely carnivorous, but in a ier stage of preparation.

t is natural to suppose that those parts of the frame which contain no ogen should be supplied by those constituents of the food which are from that element, such as the starch in bread and the sugar and fat ilk.

efore the food can be turned to account for the sustenance of the body, ust undergo *digestion*, that is, must be either dissolved or otherwise ced to such a form that it can be absorbed by the blood, which it mpanies into the lungs to undergo the process of *respiration*, and thus ecome fitted to serve for the *nutrition* of the various organs of the y, since these have to be continually repaired at the expense of the stituents of the blood.

The first step towards the digestion of the
effected by the teeth, with the aid of the *saliv*
reduced to a pulpy mass. The saliva is an alka
the presence of a peculiar albuminous substance
spit), which easily putrefies. The action of
doubtless in great part a mechanical one, bu
alkalinity assists the process chemically, by pa
portions of the food. The liability of ptyaline t
supposition that it may act in some way as a
digestion.

This disintegration of the food is of course
cooking to which it has been previously subje
portions having been thereby softened.

The food now passes to the stomach, in whicl
at the temperature of the body (98° F.), in cont
the chief chemical agent in the digestive proces

The gastric juice, which is secreted by the
stomach, is an acid liquid, containing hydrochlo
characterised by the presence of a peculiar su
albuminous class of bodies, which is called *peps*
possesses the remarkable power of enabling
presence, to dissolve such substances as fibrine
which would resist the action of the acid al
time.

An imitation of the gastric juice may be mad
membrane of the stomach for some hours in war
acid. The acid liquid thus obtained is capable
&c., if it be maintained at the temperature o
prepared from the stomach of the pig and ot
administered medicinally in order to assist diges

The principal change which the food suffers b
juice is the conversion of the fibrinous and alb
soluble forms; the starch is also partly converte
but the fatty constituents are unchanged.

The food which has thus been partially digest
by physiologists *chyme*, and passes thence into
intestines (the *duodenum*), where it is subjected
chemical agents, the *bile* and the *pancreatic jui*

Bile consists essentially of a solution of two s
and taurocholate of soda. Both glycocholic
resinous, and do not neutralise the alkali, so
alkaline character. Another characteristic featu
large proportion of carbon which it contains.
composition $HO.C_{52}H_{42}NO_{11}$, and contains there
whilst *taurocholic acid*, $HO.C_{52}H_{44}NO_{12}S_2$, co
names of these acids have reference to the circu
respectively glycocoll and taurine, together with
nitrogen, when they are boiled with dilute hydr

$$\underset{\text{Glycocholic acid.}}{HO.C_{52}H_{42}NO_{11}} + HO = \underset{\text{Cholo}}{C_{48}H_{}}$$

$$\underset{\text{Taurocholic acid.}}{HO.C_{52}H_{44}NO_{12}S_2} + 2HO = \underset{\text{Tauri}}{C_4H_7NO}$$

Taurine forms colourless crystals of great beauty, and is remarkable for the large proportion (above 25 per cent.) of sulphur which it contains. It also presents an interesting example of a complex animal derivative, which may be artificially prepared in a very simple manner.

When olefiant gas is passed over anhydrous sulphuric acid, it is absorbed, and if the product be dissolved in water, neutralised with ammonia and evaporated, crystals of *isethionate of ammonia* are obtained—

$$C_4H_4 + 2SO_3 + NH_3 + 2HO = \underset{\text{Isethionate of ammonia.}}{NH_3.HO.C_4H_5S_2O_7}.$$

When this salt is moderately heated, it loses two equivalents of water, and leaves taurine—

$$\underset{\text{Isethionate of ammonia.}}{NH_3.HO.C_4H_5S_2O_7} - 2HO = \underset{\text{Taurine.}}{C_4H_7NO_6S_2}.$$

Another characteristic ingredient of the bile is *cholesterine** ($C_{52}H_{44}O_2$), a crystalline substance somewhat resembling the fats, and often deposited in large quantity in the form of biliary calculi. It has also been found in peas, wheat, and some vegetable oils.

The peculiar colouring matter of the bile has never been obtained in a pure state.

A peculiar substance called *glycogen*, or *animal starch* ($C_{12}H_{10}O_{10}$), has been found in the liver, and becomes speedily converted into sugar after death, by assimilating the elements of water.

The special function of the bile in the digestion of the food has not been explained, but from its strongly alkaline reaction it does not appear improbable that it assists in the digestion of fatty substances.

The *pancreatic juice* is another alkaline secretion, which differs from the bile in containing a considerable quantity of albumen, and is very putrescible. Its particular office in digestion appears to consist in promoting the conversion of the starchy portions of the food into sugar (p. 496), though it also has a powerful action upon the fats, causing them to form an intimate mixture, or emulsion, with water, and partly saponifying them. The digestion of the starch and sugar is completed by the action of the *intestinal fluid* in the further passage of the food through the intestines, so that when it arrives in the small intestines, all the soluble matters have become converted into a thin milky liquid called *chyle*, which has next to be separated mechanically from the insoluble portions, such as woody fibre, &c., which are excreted from the body.

This separation is effected in the small intestines by means of two distinct sets of vessels, one of which (the *mesenteric veins*) absorbs the dissolved starchy portions of the food, and conveys them to the liver, whence they are afterwards transferred to the right auricle of the heart. The other set of vessels (*lacteals*) absorbs the digested fatty matters, and conveys them, through the thoracic duct, into the subclavian vein, and thence at once into the right auricle of the heart.

From the right auricle this imperfect blood passes into the right ventricle of the heart, and is there mixed with the blood returned from the body by the veins, after having fulfilled its various functions in the system. The mixture, which has the usual dark-brown colour of venous blood, is next forced, by the contraction of the heart, into the lungs, where it is distributed through an immense number of extremely fine vessels traversing the lungs, in contact with the minute tubes con[illegible]g

* From χολή, *bile*; στέαρ, *fat*.

the inspired air, so that the venous blood is o
by very thin and moist membranes. Through t
venous blood gives up the carbonic acid with wh
by the oxidation of the carbon of the organs, in
body, and acquires, in return, about an equal
converts it into the bright crimson arterial blood
to the left side of the heart, whence it is convey
different organs of the body.

The chemistry of the changes effected and su
circulation through the body is very imperfectl
great offices is the supply of the oxygen nece
ponents of the various organs, and thus to evolv
the body at its high temperature. The results
organs are undoubtedly very numerous; amo
carbonic (CO_2), sulphuric (SO_3), phosphoric (PO
($C_5H_4O_3$), and uric ($C_{10}H_2N_4O_3$) acids, as well as
other substances. The destroyed tissues must at
by the deposition, from the blood, of fresh parti
have been oxidised. In the course of the bloo
the above products of oxidation have to be remo
acid by the lungs and skin—the sulphuric, p
and the urea, by the kidneys.

The various liquid secretions of the body, su
the gastric juice, &c., have also to be elaborated
circulation through the arteries, after which it
the heart, to have its composition restored by
the food, and to be reconverted into arterial blo

When it is remembered that the body is ex
variations of external heat and cold, a question
made for maintaining it at its uniform temp
through the agency of the fat which is deposite
body. Since fatty substances in general are
and hydrogen, their oxidation within the body
the production of more heat than that of those
contain much nitrogen and oxygen. Accordi
exposed to a low temperature, a larger quantity
the oxidising action of the blood, and a cor
place in the amount of heat evolved, thus cor
loss of heat suffered by the body in the cooler a
cold weather, when more oxygen is required to
frame, a larger quantity of that gas is inhaled
of the higher specific gravity of the air, in addi
quickened respiration which always attends exp

To supply this extra demand for carbon and
we instinctively have recourse to such substance
which contain those elements in large proportio
from nitrogen, are often spoken of as the *respir*
whilst flesh, gluten, albumen, &c, which contai
plastic elements of nutrition (*πλάσσω, to form*).

Bearing in mind that the food has a twof
frame and to maintain the animal heat—it will b
regulated diet will contain due proportions of
tuents, such as albumen, fibrine, and caseine.

ıste of the organs, and of such non-nitrogenised bodies as starch and gar, from which fat may be elaborated to sustain the bodily warmth.

The proportion which these two parts of the food should bear to each her will, of course, depend upon the particular condition of existence the animal. Thus, for a growing animal, a larger proportion of the trogenised or plastic portion of food would be required than for an ımal whose growth had ceased; and animals exposed to a low tempera- re would require more of the non-nitrogenised or heat-giving portions of ıe food.

Accordingly we find that a man can live upon a diet which contains s in the case of wheaten bread) five parts of non-nitrogenised (starch ıd sugar) to one part of nitrogenised food (gluten); whilst an infant, hose increasing organs require more nitrogenised material, thrives upon ilk, in which this amounts to one part (caseine) for every four parts of ıe non-nitrogenised portion (milk-sugar and fat).

The inhabitants of cold climates consume, as is well known, much ıore oil and fat than those of the temperate and hot regions.

An examination of the composition of different articles of food affords s an explanation of the custom which experience has warranted, of asso- iating particular varieties of food. Thus, assuming as our standard of omparison the composition of bread, which contains one of nutritive to ıve of heat-giving matter, the propriety of associating the following kinds f food will be appreciated :—

	Nutritive.	Heat-giving.
Beef,	1	1·7
Potatoes,	1	10
Ham,	1	3
Veal,	1	0·1
Mutton,	1	2·7
Rice,	1	12·3

All muscular or mental exertion is attended with a corresponding xidation of the tissues of the frame, just as each movement of a steam- ngine may be traced to the combustion of a proportionate quantity of oal under the boiler; and hence such exertion both creates a demand or food, and quickens the respiration to obtain an increased supply of xygen.

Experiment has proved that the proportion which the oxygen consumed n respiration bears to the carbonic acid exhaled, depends very much upon he nature of the food. Thus an animal fed upon vegetable matters, such s starch and sugar (the oxygen in which exactly suffices to convert the ıydrogen into water), will turn nearly all the inspired oxygen to account n the formation of carbonic acid, the volume of which will be nearly qual to that of the oxygen which disappears at each inspiration; but when lesh, or particularly fat, is consumed, much more of the inspired oxygen s required to convert the hydrogen of the food into water, so that the olume of the carbonic acid is far less than that of the oxygen consumed n respiration. When an animal has been kept for a length of time vithout food, the proportion between the volume of the carbonic acid nd that of the oxygen consumed, is the same as if the animal were being ed upon a flesh diet, inasmuch as its own flesh alone is now supporting *ts respiration.*

CHANGES IN THE ANIMAL BODY AFTER DEATH.

453. After the death of animals, just as after that of plants, their component parts are reduced to the primary forms from which they were derived, so that they may begin again at the foot of the ascending scale of life. Very soon after life is extinct, the atmospheric oxygen begins to induce a change in some of the nitrogenous constituents, and this change is soon communicated to all parts of the body, which undergo a putrefaction or metamorphosis, of which the ultimate results are the conversion of the carbon into carbonic acid, the hydrogen into water, the nitrogen into ammonia, nitrous and nitric acids, and the sulphur into sulphuretted hydrogen and sulphuric acid. The mineral constituents of the animal frame then mingle with the surrounding soil, and are ready to take part in the nourishment of plants, which construct the organic components of their frames from the carbonic acid and ammonia furnished by the putrefaction of the animal, and then serve in their turn as sustenance for animals whose respiration supplies the air with carbonic acid, and takes in exchange the oxygen eliminated by the plant.

The functions of the two divisions of animate nature are, therefore, perfectly reciprocal, and this relationship must be regarded as the foundation of economical agriculture.

If it were possible to prevent the change of the atmosphere, it is quite conceivable that a perpetual succession of plants and animals could be raised upon a given farm without any importation of food, provided that there was also no exportation. Or even, permitting an exportation of food, the succession of plants and animals raised upon the same land might be, at least, a very long one, if the solid and liquid excrements of the animals, to feed whom this exportation took place, were restored to the land upon which this food was raised. The explanation of this is, that the solid and liquid excrements of the animal contain a very large proportion of the mineral constituents of the soil, in the very state in which they are best fitted for assimilation by the crop, and as long as the soil contains the requisite supply of mineral food, the plant can derive its organic constituents from the atmosphere itself.

Forasmuch, however, as the vegetable and animal food produced upon a farm is generally exported to feed the dwellers in towns, whose excrements cannot, without excessive outlay, be returned to the soil whence the food was derived, it becomes necessary for the agriculturist to purchase farm-yard manure, guano, &c., in order to prevent the exhaustion of his soil. A great manufacturing country, in which the majority of the inhabitants are congregated in very large numbers around a few centres of industry, at a distance from the land under tillage, is thus of necessity dependent for a considerable proportion of its food upon more thinly populated countries where manufactures do not flourish, to which it exports in return the produce of the labour which it feeds.

The parts of the frames of animals differ very considerably in their tendency to putrefaction. The blood and muscular flesh undergo this change most readily, as being the most complex parts of the body, whilst the fat remains unchanged for a much longer period, and the bones and hair will also resist putrefaction for a great length of time.

The comparative stability of the fat is observed in the bodies of animals which have been buried for some time in a very wet situation, where the

are often found converted almost entirely into a mass of *adipocere*, consisting of the stearic and margaric acids derived from the fat.

When an animal body is thoroughly dried, it may be preserved unchanged for any length of time, and this is the simplest of the methods adopted for the preservation of animal food, becoming far more efficacious when combined with the use of some antiseptic substance such as salt, sugar, spice, or kreasote.

The preservative effects of salt and sugar are sometimes ascribed to the attraction exerted by them upon moisture, which they withdraw from the flesh, whilst spices owe their antiseptic power to the essential oils, which appear to have a specific action in arresting fermentative change, a character which also belongs to kreasote, carbolic acid, and probably to other substances which occur in the smoke of wood, well known for its efficacy in *curing* animal matter.

A process commonly adopted for the preservation of animal and vegetable food consists in heating them with a little water in tin canisters, which are sealed air-tight as soon as the steam has expelled all the air, and if the organic matter be perfectly fresh, this mode of preserving it is found very successful, though, if putrefaction has once commenced, to ever so slight an extent, it will continne even in the sealed canister, quite independently of the air.

Modern experiments have disclosed a great imperfection in our acquaintance with the conditions under which putrefaction takes place, and appear to indicate the presence in the atmosphere of some minute solid particles which appear to be minute ova or germs, and have the power of inducing the commencement of this change. It has been found that milk, for example, may be kept for a very considerable period without putrefying, if it be boiled in a flask, the neck of which is afterwards loosely stopped with cotton wool, whilst, if the plug of cotton wool be omitted, the other conditions being precisely the same, putrefaction will take place very speedily.

Perfectly fresh animal matters have also been preserved for a length of time in that state, in vessels containing air which has been passed through red-hot tubes with the view of destroying any living germs which might be present, and such substances have been found to putrefy as soon as the unpurified air was allowed access to them.

The extremes of the scale of animated existence would appear to meet here. The highest forms of organised matter, immediately after death, serve to nourish some of the lowest orders of living germs, which help to resolve the complex matter into the simpler forms of carbonic acid, ammonia, &c., which are returned to the atmosphere, the great receptacle for the four chief elements of living matter.

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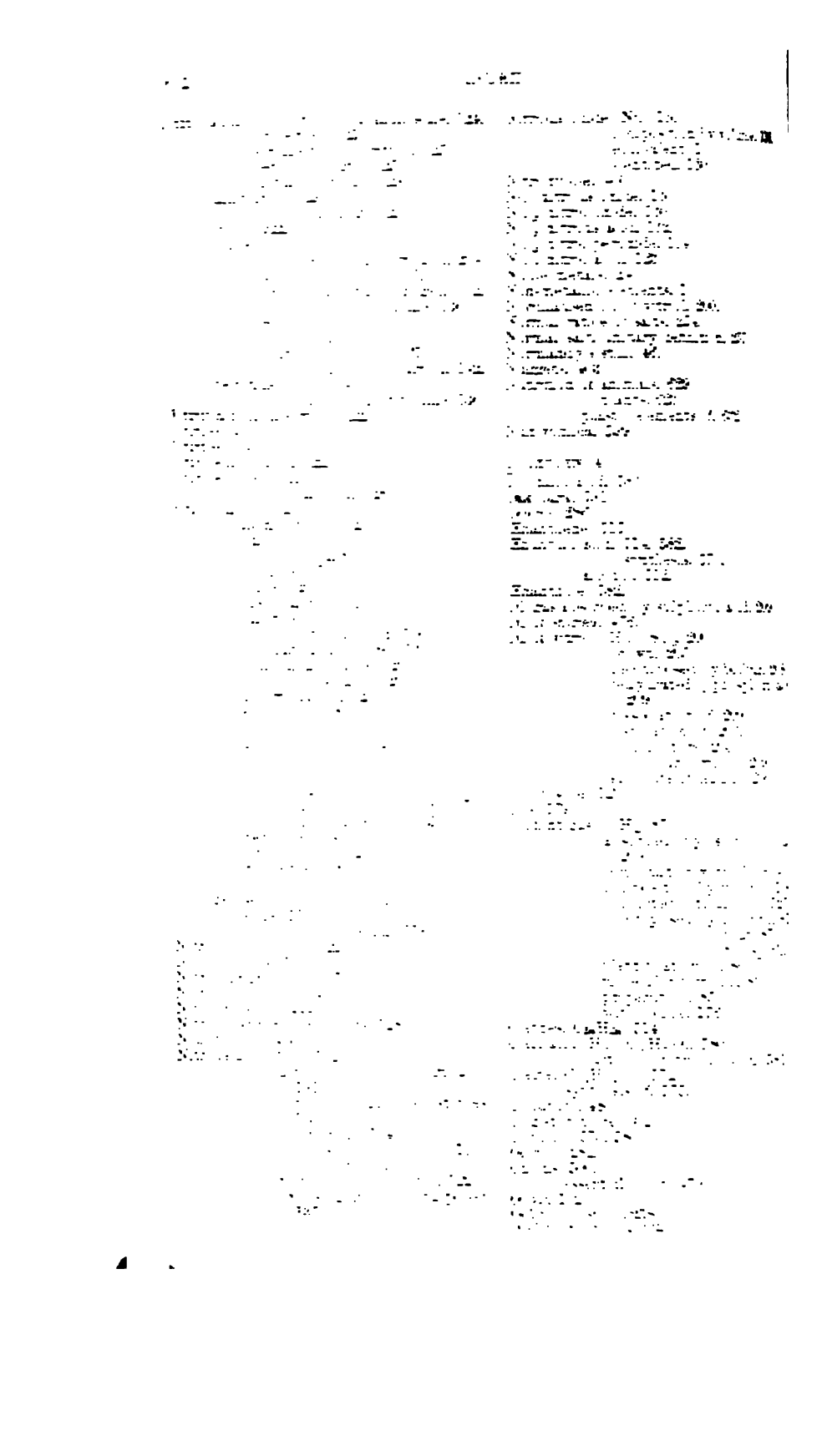

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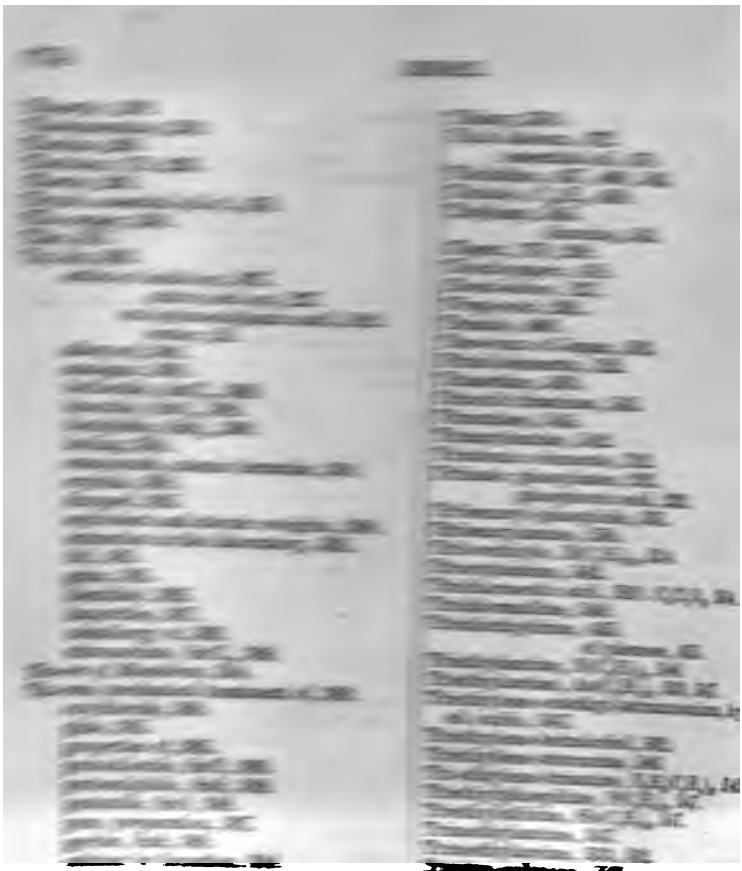

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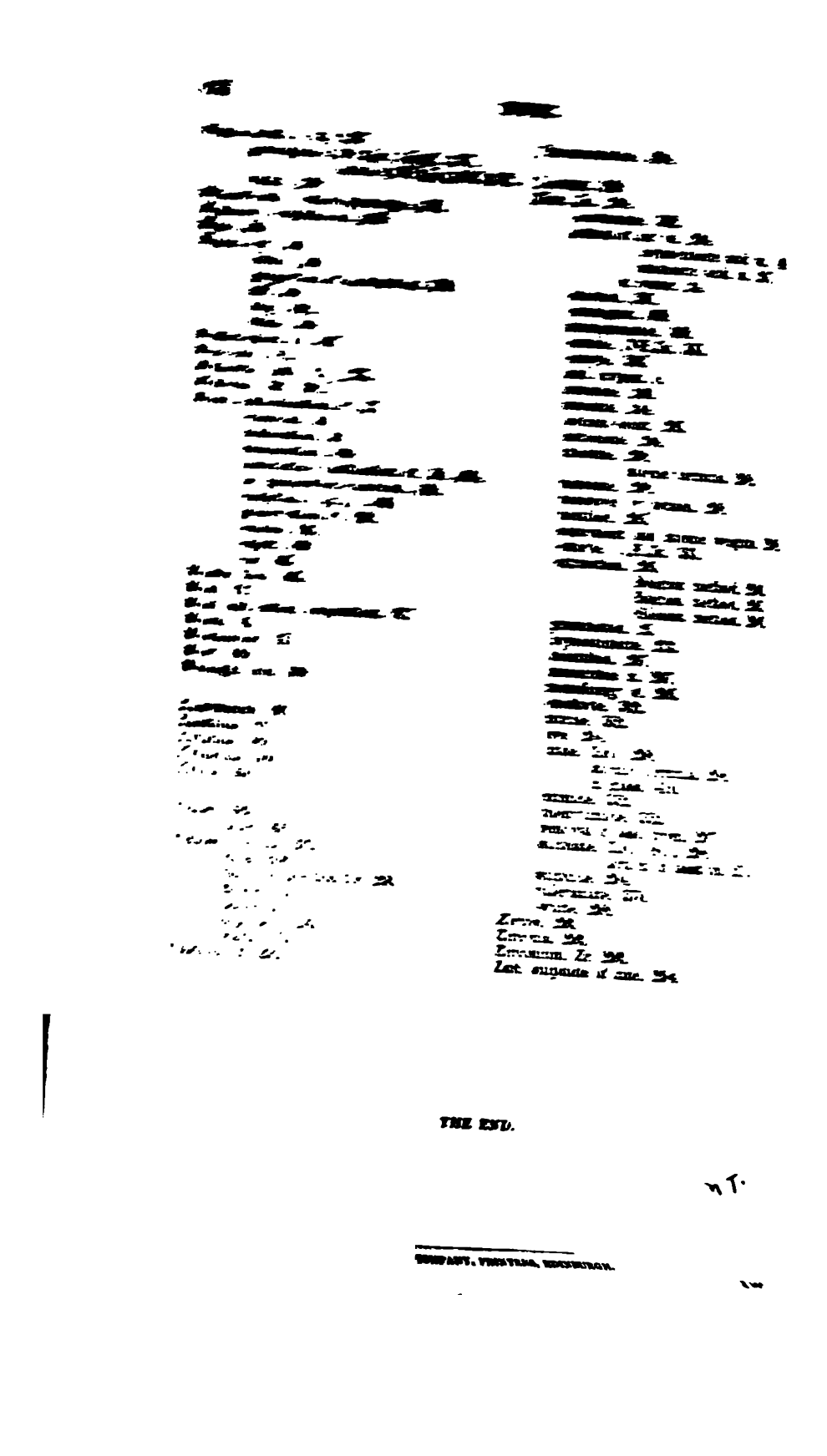

THE END.

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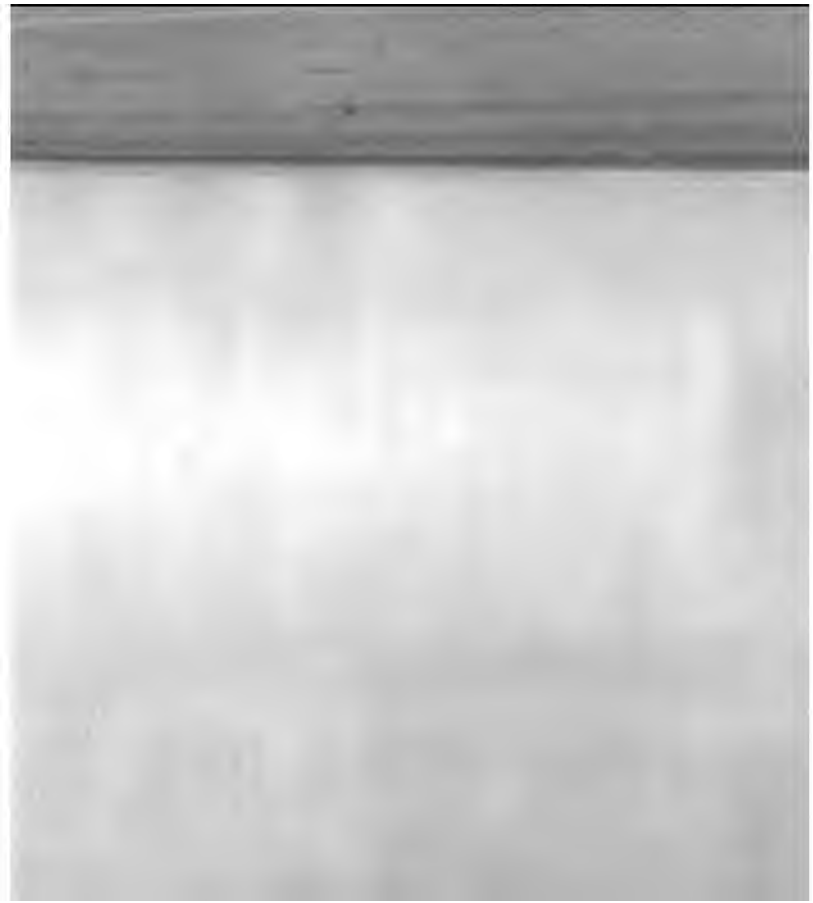

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